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Carbon Monoxide Rich Methanation Kinetics on Supported Rhodium and Nickel

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Approved for public release; distribution unlimited

A thesis submitted to the University of Houston, Houston, TX 77004 in partial fulfilment of the requirements for the degree of Master of Science; Chemical Engineering.

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Dedicated to my wife Joan.

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CARBON MONOXIDE RICH METHANATION KINETICS ON SUPPORTED RHODIUM AND NICKEL CATALYSTS

A Thesis

Presented to

The Faculty of the Department of Chemical Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemical Engineering

By

Daniel Keehan

August 1988

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CARBON MONOXIDE RICH METHANATION KINETICS ON SUPPORTED RHODIUM AND NICKEL CATALYSTS

An Abstract of a Thesis

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Abstract

The utilization of CO_2 reforming of methane in a solar based Chemical Energy Transmission System (CETS) relies greatly upon the development of suitable catalysts for both the endothermic and exothermic reactions. CO_2 reforming of methane produces hydrogen and carbon monoxide at a ratio of about one, thus requiring the methanation reaction on the other side of the closed loop CETS to utilize this feed. H_2/CO ratios lower than three favor the formation of carbon with industrial methanation catalysts. Preliminary tests performed on methanation with rhodium and nickel catalysts produced two, 0.5% Rh/Al_2O_3 and 70% Ni/Al_2O_3, for further study.

Kinetic experiments were conducted in an isothermal continuous stirred tank reactor constructed of a copper alloy which prevented carbon formation on reactor parts. These experiments were performed on pelleted 0.5% Rh/Al_2O_3 in the 400 to 500°C range and pelleted 70% Ni/Al_2O_3 in the 300 to 500°C temperature range. In most experiments steam was added to the reactor feed to inhibit carbon formation. Langmuir-Hinshelwood expressions were fitted to experimental data for both catalysts and are suitable for reactor design purposes.

Lifetime studies, at high CO conversion, were conducted with both catalysts.The catalyst, 0.5% Rh/Al_2O_3, resists carbon formation very well and is recommended for application at temperatures above 400°C. The nickel-containing catalyst, 70% Ni/Al_2O_3, has a high carbon formation resistance at temperatures below 350°C and is suitable for application in the 300 to 350°C temperature range.

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CHAPTER 1

INTRODUCTION

A Chemical Energy Transmission System (CETS) [1] is a process for storing energy from a main energy source in the form of chemical binding energy through a reversible endothermic reaction. This stored energy is transported through a pipe line to a location where the energy is released, via the reverse exothermic reaction, for public or industrial consumption (Figure 1.1). The energy to drive the endothermic storage reaction comes from either fossil fuels, nuclear fuel, or the sun. Of these energy sources, the sun is the least expensive and the cleanest. With the present fossil fuel situation, industry is finding more direct applications for carbon based fuels as raw materials in specialty chemical production, which makes them more valuable as a raw material than as a heat generating fuel. Use of nuclear fuel as an energy source grows more difficult each day due to increased cost of the fuel, difficulty and expense of disposing of process waste, and rising public and governmental regulation of the industry. In West Germany a nuclear based CETS, the EVA-ADAM [2],was constructed for experimental purposes. The success of this experimental unit demonstrated that steady-state operation of a CETS is possible. The work presented in this thesis was done in support of the design and development of a solar based CETS by the Sandia National Laboratories, Albuquerque, New Mexico.

1.1 Solar CETS

In order for any CETS to be successful, the right energy storage/release reaction must be chosen. The primary criterion a reaction must meet is that it must be reversible and have high conversions in the temperature range covered by the CETS. For a solar based

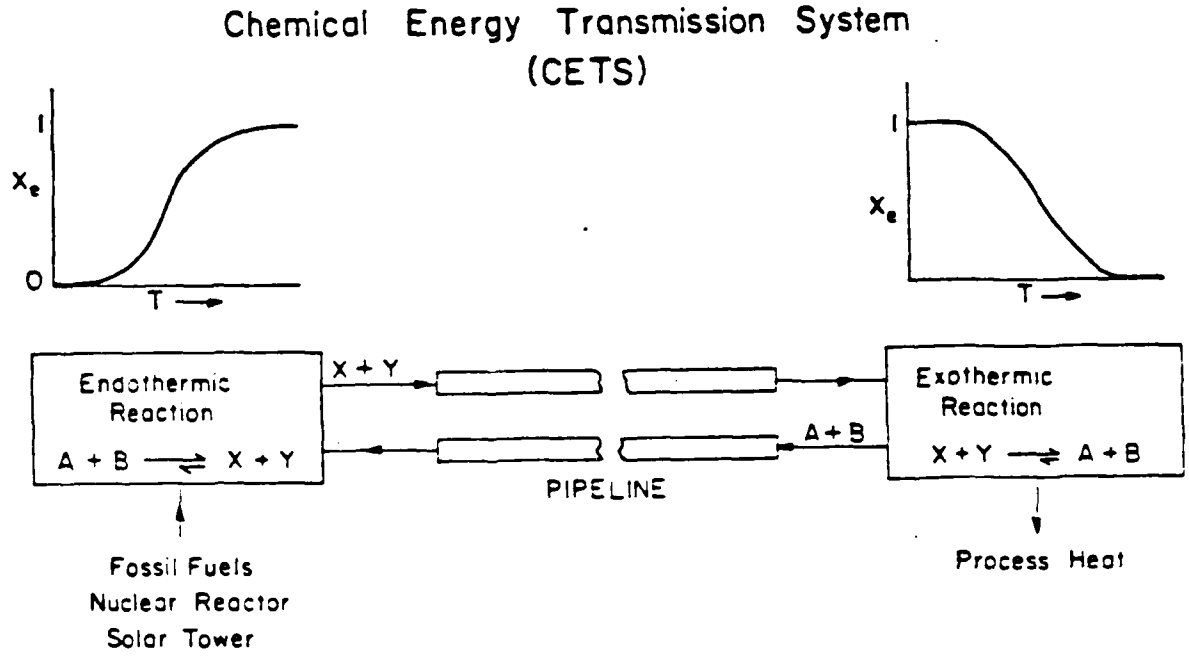


Figure 1.1
Schematic CETS [1]

CETS the endothermic reaction is carried out at between 800 and 1200°C and the exothermic reaction between 300 and 550°C. The reaction also must be catalyticaly induced so the reaction can be controlled. Of the many reactions known, five were chosen as the most promising [1] (Table 1.1). Additional conditions must be met: 1) the reaction should have a high transmission capacity, i.e., energy transferred per gram of reactants, 2) there must be no side reactions producing contaminants that accumulate in the closed loop, 3) the reaction must not generate or consume compounds which are toxic, corrosive, or explosive, and 4) the reaction should be one which has been developed industrially, thus avoiding extensive work on basic technology.

Table 1.1

CETS Reactions [1]

Chemical Reaction	kJ g^{-1}	
$CH_4 + H_20 \Leftrightarrow CO + 3H_2$	6.06	{1.1}
$CH_4 + CO_2 \Leftrightarrow 2CO + 2H_2$	4.12	{1.2}
$2NH_3 \Leftrightarrow N_2 + 3H_2$	3.86	{1.3}
$C_6H_{12} \Leftrightarrow C_6H_6 + 3H_2$	2.84	{1.4}
$2SO_3 \Leftrightarrow 2SO_2 + O_2$	1.52	{1.5}

Of the reactions in Table 1.1, steam reforming of methane, {1.1}, is the most promising [1]. Steam reforming of methane is an established process in the chemical industry. Catalyst and reactor technology is advanced and has been proven. High conversions have been obtained for the endothermic reforming reaction, and catalysts and technology exist for methanation to produce a high temperature exothermic reaction [3,4]. The main problem with steam reforming is the formation of carbon on the catalyst. This occurs by one of two reactions:

$$CH_4 \Leftrightarrow C + 2H_2 \qquad \{1.6\}$$

$$2CO \Leftrightarrow C + CO_2 \qquad \{1.7\}$$

The equilibrium constants for these reactions are shown in Figure 1.2, and are measured for nickel catalysts [5]. Reaction {1.6} is favored at high temperatures such as those encountered in a methane reformer, whereas Reaction {1.7} is favored at lower temperatures found in methanators. The problem of carbon formation in the reformer can be solved by using two to three times the stoichiometric amount of steam in the feed to the reformer [3,6]. This removes the carbon by the reaction,

$$C + H_20 \Leftrightarrow CO + H_2 \qquad \{1.8\}$$

Carbon formation in the methanator can be halted by using excess hydrogen in the feed to drive the reaction [3],

$$H_2 + C \Leftrightarrow CH_4 \qquad \{1.9\}$$

The next most promising reaction is CO_2 reforming of methane, {1.2}. This reaction has a high transmission capacity and is reversible with high conversion over the operating temperatures encountered in a solar based CETS. The main problem with CO_2 reforming is that little commercial use has been made of this reaction, and there are no proven catalysts and reactor technology. With present commercially available reforming catalysts, severe coking occurs on the catalyst [7,8]. Without steam in the feed, Reaction {1.6} is not countered by Reaction {1.8}. This leads to rapid deactivation of the commercial nickel catalysts by coke formation. Excess CO_2 can be added to the feed of the reformer to suppress Reaction {1.7}, but the excess CO_2 in the product stream suppresses the methanation reaction. Also CO_2 reforming of methane produces a product stream in which the H_2/CO ratio is about one. This low ratio causes severe coking on presently available methanation catalysts [4]. Steam reforming and CO_2 reforming appear to be similar processes thus some of the reactor technology developed for steam reforming could be applied to CO_2 reforming. The principal obstacle left in the application of CO_2 reforming to a solar based CETS is the development of catalysts which resist carbon formation under the reforming and methanation reactor conditions.

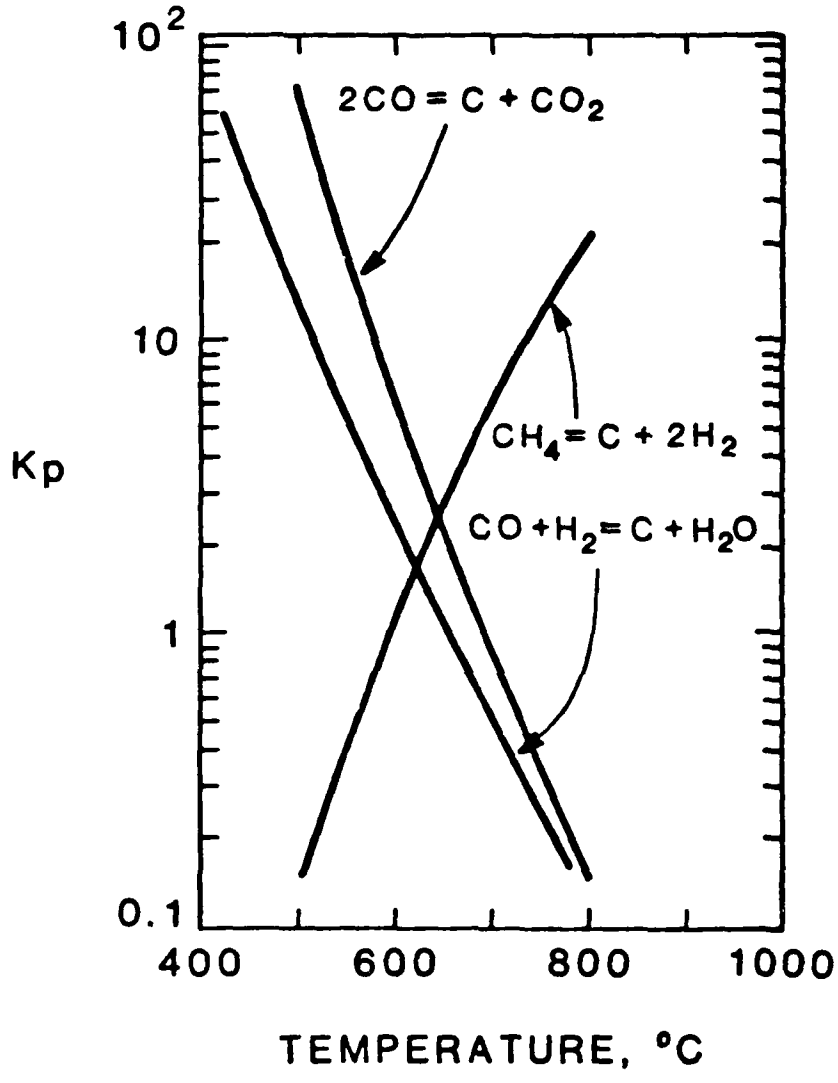


Figure 1.2
Equilibrium Constants For Carbon Formation Reactions [5]

Ammonia synthesis (Reaction {1.3}) is an exothermic reaction favored at high pressures [9]. For high conversion the reactor must be operated at low temperature and high pressure with recycle. Typical ammonia reactors operate at 200 to 300 bar and 400 to 500°C. The considerable amount of compression for reactor pressure and recycle tends to discourage use of ammonia synthesis as an economical candidate for a chemical storage reaction in a solar based CETS.

Hydrogenation of benzene (Reaction {1.4}) on an industrial scale is a very efficient process [9]. Catalyst and reactor technology for this reaction have been proven. The main concern about the use of this reaction is the toxicity of both benzene and cyclohexane. These chemicals are handled commercially every day, but the danger involved in long distance pipe line transmission makes this reaction unsuitable for the solar CETS.

Oxidation of sulfur dioxide (Reaction {1.5}) was found to be a very promising reaction [10]. The reaction is endothermic at atmospheric pressure and has no side reactions. The reverse reaction has been chemically proven in the industrial production of sulfuric acid. Difficulty with this reaction arises because of the corrosive nature of SO_3 whose interaction with various metals has not been thoroughly studied. These metallurgical problems preclude the immediate use of the oxidation of sulfur dioxide in a solar based CETS.

For solar CETS there are two types of receivers being considered. There is the central receiver system (Figure 1.3) and the distributed receiver system (Figure 1.4). With both, the use of steam reforming causes difficulty, since two to three times the stoichiometric amount of steam must be added to the reformer feed to suppress carbon formation on the catalyst. In both cases this steam must be generated on site, which is possible via solar energy, but all the steam in the product stream must also be condensed before the process gases can be transported at ambient conditions to the methanator. Some of the steam could be used to operate the reforming facility, but much would be wasted. With the distributed receiver system, the additional problem of insulating or heating the

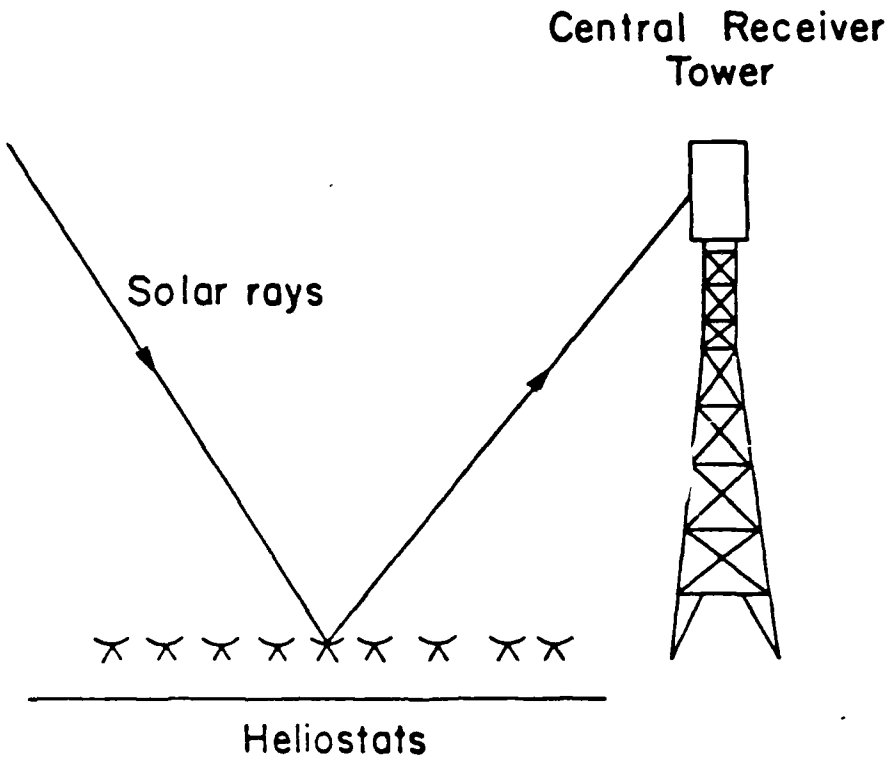


Figure 1.3
Central Receiver System [1]

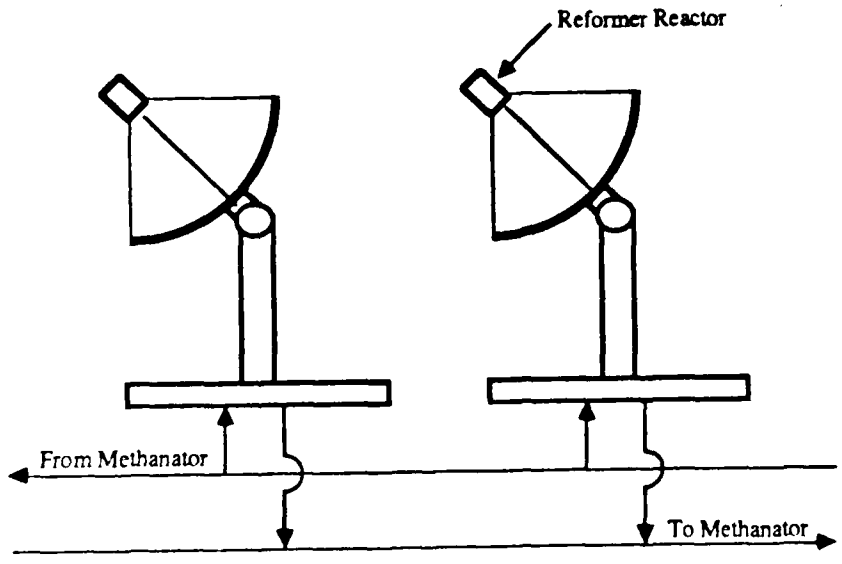


Figure 1.4
Distributed Dish Receiver

interconnecting lines to prevent condensation of the steam arises. This increases both capital investment and operation cost.

An obvious solution is to eliminate steam in the reformer. This could be accomplished with CO_2 reforming of methane {1.2}. However, use of CO_2 reforming requires extensive research on the development of suitable catalysts and on the kinetics of the CO_2 reforming reaction. Much of this work has been undertaken by Richardson and coworkers at the University of Houston [7].

1.2 Methanation

Equally important is the question of the methanation side of the solar based CETS. Methanation is a technically proven industrial process [4]. Today there are three main applications: 1) elimination of CO from fuel gases to produce methane rich, high Btu value fuels, 2) elimination of CO from feed gases in such processes as ammonia synthesis to prevent catalyst poisoning, 3) production of Synthetic Natural Gas (SNG) from naphtha or coal. Over the past 80 years, many studies have been conducted on catalytic methanation. Summaries of this work are found in [4,11,12,13].

The nuclear based CETS, the EVA-ADAM, utilized steam reforming of methane in EVA to store nuclear generated thermal energy, and methanation in ADAM to release the stored chemical energy [1]. The EVA-ADAM and the second generation unit, EVAII-ADAMII, were not designed to be highly efficient but rather to be flexible so that many studies could be conducted on the one unit. Since the goal was research and not efficiency, use of steam reforming and excess steam in the process was not of as great a concern as it would be in a solar based CETS. EVA-ADAM demonstrated that a CETS can be operated successfully, but for a solar-based CETS more care must be placed in the over-all process design.

The methanator, ADAM, consisted of three adiabatic methanation reactors packed with a nickel catalyst, each followed by heat exchangers (Figure 1.5). Due to the highly exothermic nature of the methanation reaction, the feed stream to the first methanator was diluted and the reaction carried out in three stages to prevent sintering of the nickel catalyst. The first methanator was operated at an exit temperature of 600°C,. and the last at about 300°C. No problems were reported with the nickel catalysts. Carbon formation was not expected since steam reforming produces H_2 and CO in a ratio higher than 3:1. For a solar CETS using CO_2 reforming, the methanation catalyst must resist coking at H_2/CO ratios of about one, for successful methanator operation.

Methanation is a highly exothermic reaction. Table 1.2 shows the other reactions which accompany Reaction {1.10}. As pointed out by Mills et al. [4], the hydrogenation of CO_2 {1.11} does not occur when CO is present, thus Reaction {1.11} can be eliminated from the competing reactions in the methanator since there will always be CO present. It should also be noted that the water-gas shift reaction {1.12} is not strongly exothermic and does not compete as strongly with Reaction {1.10} for CO. The reaction which competes the most and causes the most problem is the Boudouard reaction {1.7}. This reaction is one of the main causes of methanation catalyst failure and has been the topic of study for many researchers [3,4,6].

As mentioned earlier, the deposition of carbon on the catalyst can be reduced or eliminated by having a H_2/CO ratio greater than three. Operation of many commercially available methanation catalysts below a H_2/CO ratio of three results in carbon formation (Figure 1.6) [4,6]. Since no catalyst exist for such low ratios and it is not feasible to inject H_2 into the closed-loop CETS, the only alternative is to develop a catalyst which does not produce carbon at H_2/CO ratios of about one. Such ratios will be encountered in the methanator of the CO_2 reforming solar-based CETS.

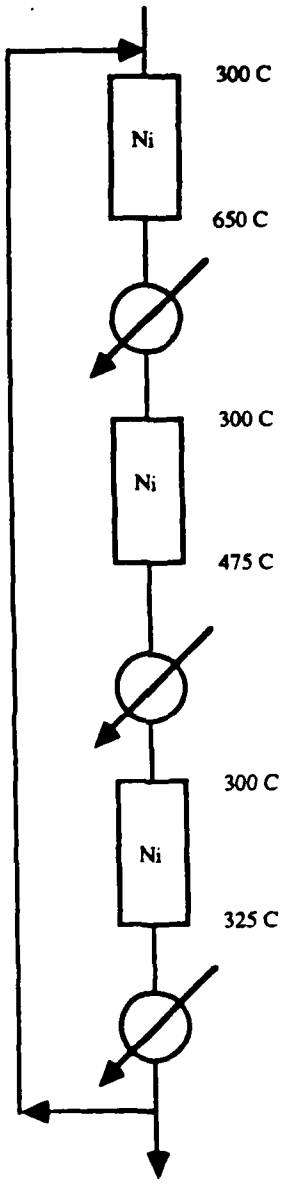


Figure 1.5
ADAM Methanator Configuration

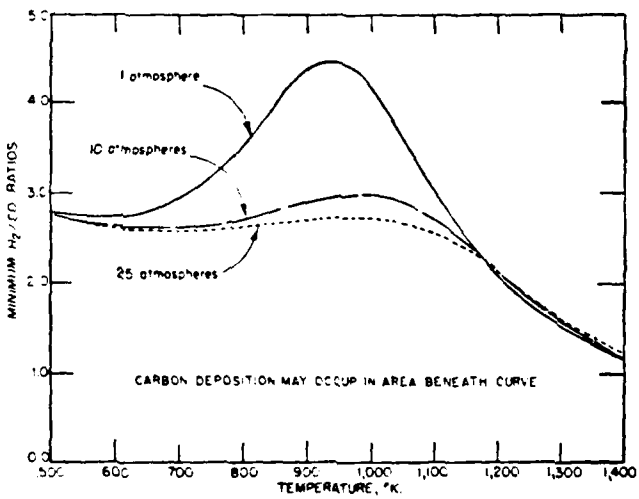


Figure 1.6
Carbon Deposition Boundaries [11]

Table 1.2

Reactions Associated With Methanation [4]

Chemical Reaction	$\Delta H_{r400°C}$ (kcal mol^{-1})	
$3H_2 + CO \Leftrightarrow CH_4 + H_2O$	-50.36	{1.10}
$4H_2 + CO_2 \Leftrightarrow CH_4 + 2H_20$	-40.65	{1.11}
$CO + H_2O \Leftrightarrow CO_2 + H_2$	-9.71	{1.12}
$2CO \Leftrightarrow C + CO_2$	-41.43	{1.7}

The problem of carbon formation on the methanation catalyst at low H_2/CO ratios was addressed by Richardson and Cullinane [14]. Using a rapid catalyst screening method [15], a 0.5% rhodium on alumina catalyst was discovered which catalyzed the methanation reaction, had a low activation energy, and did not promote the formation of carbon at H_2/CO ratios as low as one. The properties of this catalyst can be seen in Table 1.3. This catalyst performed very well over a range of operation conditions, but was found to be very sensitive to impurities in the feed stream, such as iron carbonyl.When contacted with the catalyst surface, the iron carbonyl decomposed and deposited iron which in turn catalyzed the carbon formation reaction. The catalyst was also sensitive to iron impurities in the alumina support. For successful use of this catalyst care must taken to eliminate all sources of contamination.

The methanator design being considered for the CO_2 reforming solar-based CETS is similar to that used in the EVA-ADAM [1], except the last methanator is operated isothermally instead of adiabatically (Figure 1.7). The reactants to the first two methanators enter at a temperature of about 350°C and exit at about 500°C. The third methanator is operated isothermally at about 300°C. At low temperatures the 0.5% Rh catalyst was found to have low activity, in fact so low that the amount of catalyst required to fill the third methanator was excessive. For this reason another catalyst with high

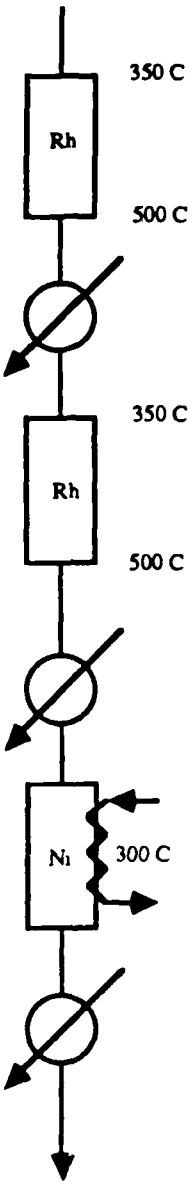


Figure 1.7
Solar CETS Methanator Configuration

activity was necessary for the third methanator. This catalyst must have a high activity at 300°C, and resist carbon formation under the methanator reactor conditions. Nickel seemed to be the best choice because of its high activity and low cost, but the right catalyst formula had to be found. The screening study [14] indicated that a proprietary methanation catalyst, used for the production of SNG from naphtha and coal gasification, was suitable at temperatures below 400°C. The catalyst contained 70% Ni and greater than 1% K on an alumina support. The catalyst was known to resist carbon formation in conventional SNG processes, but had to be tested under the reaction conditions that would be encountered in the methanator.

Table 1.3

Properties of 0.5% Rh Catalyst [16]

Commercial Nomenclature	Engelhard 3253702, 0.5% Rh on 1/8" Alumina Pellets
Measured Rhodium wt.%	0.488
Support Surface Area, m^2g^{-1}	90
Pellet Density, g cm^{-3}	1.75
Bulk Density, g cm^{-3}	1.04
Pore Volume, cm^3g^{-1}	0.35
Mean Mesopore Radius, Å	30
Mean Macropore Radius, Å	3000
Rhodium Surface Area, m^2g^{-1} (Rh)	188
Approximate "egg-shell" Thickness, cm	0.01

1.3 Objectives

Screening tests indicated the suitability of rhodium and nickel catalysts for high and low temperature applications respectively. This thesis describes the determination of kinetic expressions for the rate of methanation on both the 0.5% Rh and 70% Ni catalysts in their pelleted state, and testing for extended periods of time at actual operating conditions to determine their durability and suitability for this application.

CHAPTER 2

EXPERIMENTAL EQUIPMENT

The purpose of the research conducted during this study was to determine the rate equations for the methanation reaction catalyzed by both 0.5% Rh and 70% Ni catalysts. Much of the experimental equipment used was constructed and assembled by former workers. The basic design of the reactor was that of Hadjigeorghjiou [17]. Torres-Acosta [18] designed, constructed, and tested the catalyst testing unit which was later modified by Cullinane [15]. This chapter describes the equipment used and notes any changes made. For a more detailed description of the existing equipment, the three original sources should be referenced.

The description of the experimental equipment is divided into the following sections: Reactor design, gas metering and mixing, process flow, gas sampling, product analysis, and process control.

2.1 Reactor Design

In choosing the type of catalytic reactor several factors were considered. These were economics, catalyst form, ability to operate isothermally, ease of data analysis, reactions being studied, and ability to operate at both very low and high conversion. A preliminary screening of possible reactor types was conducted with the aid of the work of Doraiswamy and Tajbl [19]. A Continuous Stirred Tank Reactor (CSTR), a Packed Bed Reactor (PBR) without recycle, and a PBR with a recycle stream were considered.

The CSTR can be manufactured at moderate cost and designed to contain the 1/8" catalyst pellets used in both the rhodium and nickel studies. It could also be constructed of

a metal which was inert to the methanation reaction being studied, and to side reactions. A CSTR is also easy to control, and can be operated isothermally at both low and high conversion. Data produced by the CSTR is easy to analyze because the CSTR is assumed to be perfectly mixed, thus the concentration at the outlet is the concentration throughout the reactor. This feature allows the data to be used without further manipulation.

The PBR without recycle may also be manufactured at a low cost and can be operated at both low and high conversion, but its ability to operate isothermally depends on the size of the catalyst bed [19]. Data obtained from the reactor must be statistically analyzed to account for the differential conversion which occurs at each point along the bed, together with the temperature change which may also be present in highly exothermic reaction.

The PBR with recycle avoids some of these difficulties [19]. It may be operated differentially by recycling a large portion of the effluent stream. This requires a positive displacement pump to force the effluent gases across any pressure drop which develops in the reactor. Reducing the recycle rate allows for operation at high conversion. Isothermal operation may be possible depending upon the size of the catalyst bed and the rate of reaction. When operated in the differential mode, the data give the reaction rates directly, but when operated at a high conversion the data require extensive statistical analysis.

Of the reactors considered, the CSTR proved to be the best for this study. The simple PBR without recycle was unsuitable for the following reasons. First, isothermal operation can not be assured, which is essential for kinetic studies. Secondly, the data must be statistically analyzed before a reaction rate can be determined. This involves assumptions which lead to greater errors in the final rate expression. The PBR with recycle has the disadvantage that a positive displacement metering pump must be specially manufactured to be catalytically inert and operate at temperatures ranging from 300 to 500°C. The manufacture of such a pump is very costly. Also, at high conversion the data still needs statistical analysis. The choice of a CSTR design was simplified by the

existence of a reactor which had been designed, built, and tested by Hadjigeorghiou [17] to study high pressure methanation. The same reactor was used for these experiments after some modifications.

The original reactor was a modified 300 cm^3 Autoclave stirred pressure vessel (Figure 2.1). It was constructed of 316 stainless steel which is strong and durable, yet catalyzes the coking reaction when the hydrogen to carbon monoxide ratio falls below three. Coke deposition results mainly from the high nickel content of the steel [11]. This fact was critical because the methanation reaction must be studied at H_2/CO ratios between one and two.

Therefore, the reactor was constructed of a metal having the smallest catalytic effect in the presence of the gases produced and consumed by the reactions involved. Of the metals investigated, copper proved to be the cheapest and most catalytically inert [4]. It could also be used in the temperature and pressure ranges studied.

Initially, all parts of the reactor were to be copper plated, but it was found that copper plating is easily damaged and may even peel after several heating and cooling cycles. The next alternative was to make the reactor from pure copper. This was not feasible because pure copper is not easily machined. The final alternative was to choose a copper alloy which could be machined and yet does not contain any metals acting as catalysts. Aluminum, Silicon, Bronze (CDA# 642: 91% Cu, 7% Si, 2% Al) was chosen as a suitable alternative. Aluminum, Silicon, Bronze (ASB) had all of the desired characteristics required except it lacked the strength of 316 stainless steel. Since the original Autoclave magnetic drive system (Figure 2.2) was used, the reactor itself remained 316 stainless steel. A design compromise was to use the 316 stainless steel pressure vessel fitted with an ASB sheath, and to construct all of the internal parts of ASB.

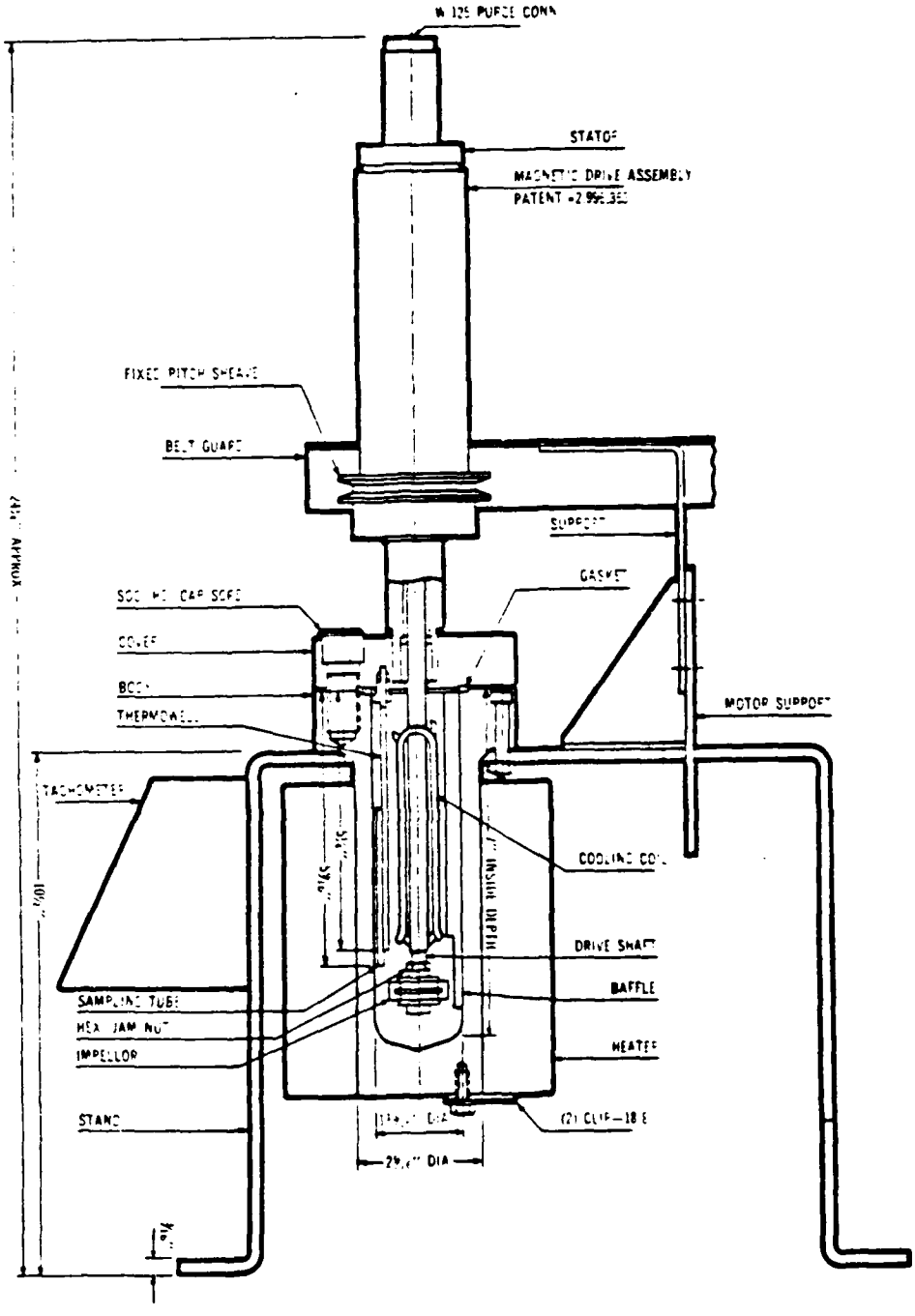


Figure 2.1
Unmodified Autoclave Pressure Vessel [20]

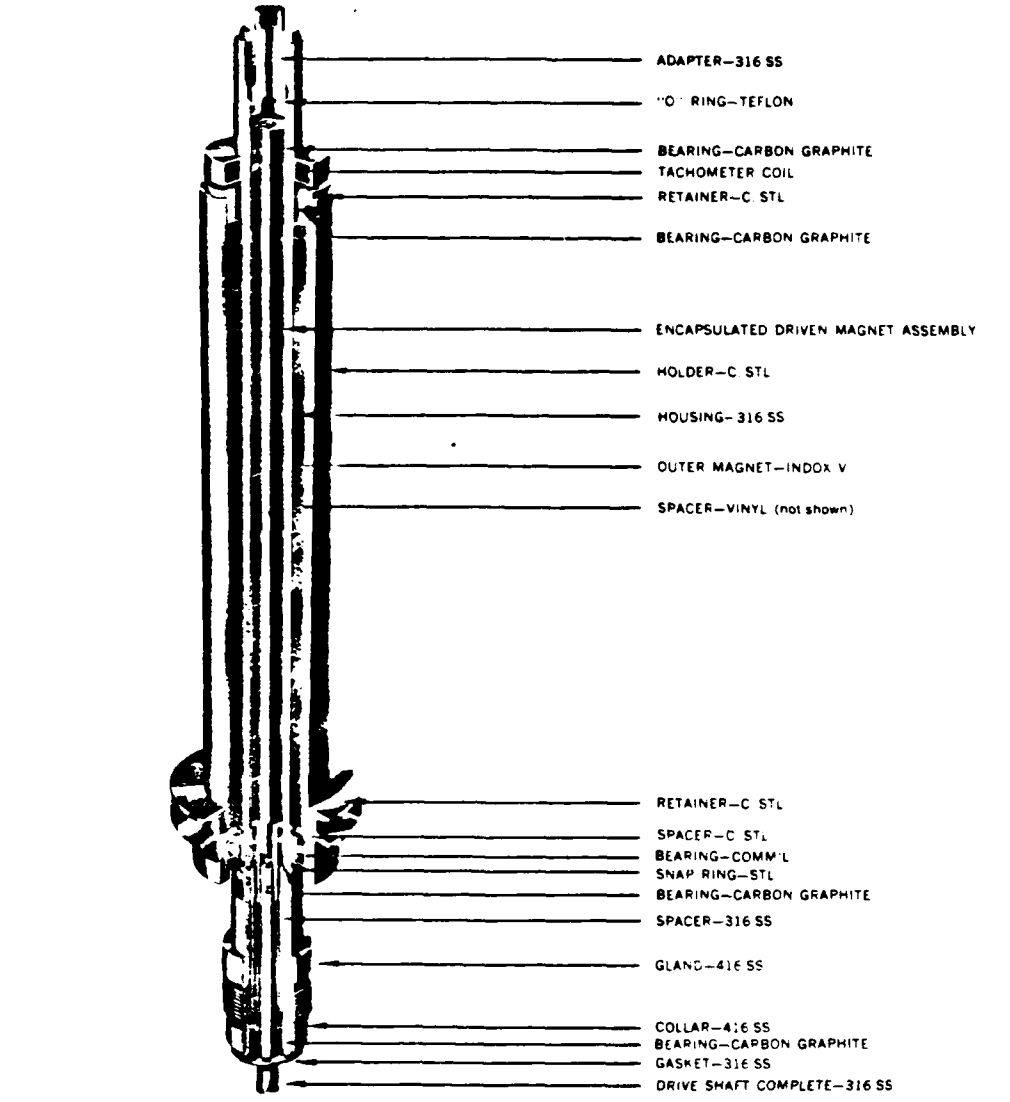


Figure 2.2
Autoclave Magnetic Drive System [20]

This solution gives mechanical strength of the 316 stainless steel yet provides a reaction environment which is catalytically inert.

Several improvements were made to the original design. First, the impeller blades were made one eighth of an inch longer. This helped improve mixing. Secondly, the ends of the basket were sealed by placing a plate on the bottom and sealing the top against the dead volume insert. This eliminated any short circuiting and achieved a better perfectly mixed state. Thirdly, flow channels were machined into both the upper and lower wire supports, thus increasing gas circulation and providing gas exits at locations far from the inlet tube. Finally, dual element, ungrounded Omega thermocouples were used to measure bed and gas temperatures. This allowed the use of one probe to obtain measurements for both the process control computer and the digital read-out box from the same location in the reactor. Schematics of reactor parts appear in Figures 2.3 to 2.7.

A Research Incorporated Model 63911 Temperature Controller maintained the desired temperature within the reactor. Initially the controller was connected to a thermocouple in the reactor bed, since this gives the best results, but it lead to large oscillations about the reactor setpoint. The oscillations were due to the lag time created by the thick walls of the pressure vessel, which slowed heat transfer. To correct this the controller was connected to a thermocouple in the reactor heating block, and gave the required temperature within one degree Celsius.

2.2 Gas Metering and Mixing

The gas metering and mixing system was comprised of eight Tylan Model FC260 Mass Flow Controllers (MFC), Eight Tomco Solenoid Shut Off Valves (SSOV), seven check valves, two Tylan Model RO 20A readout boxes, one Sage Instruments Model 220

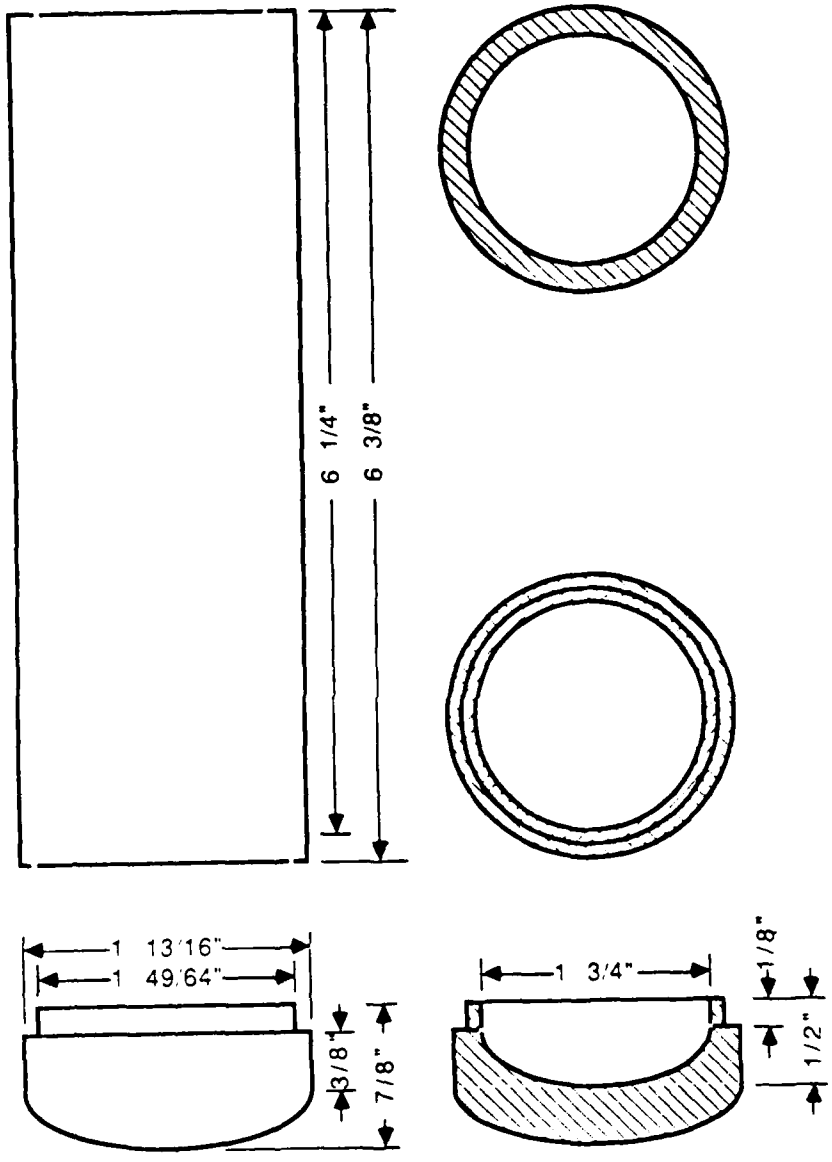
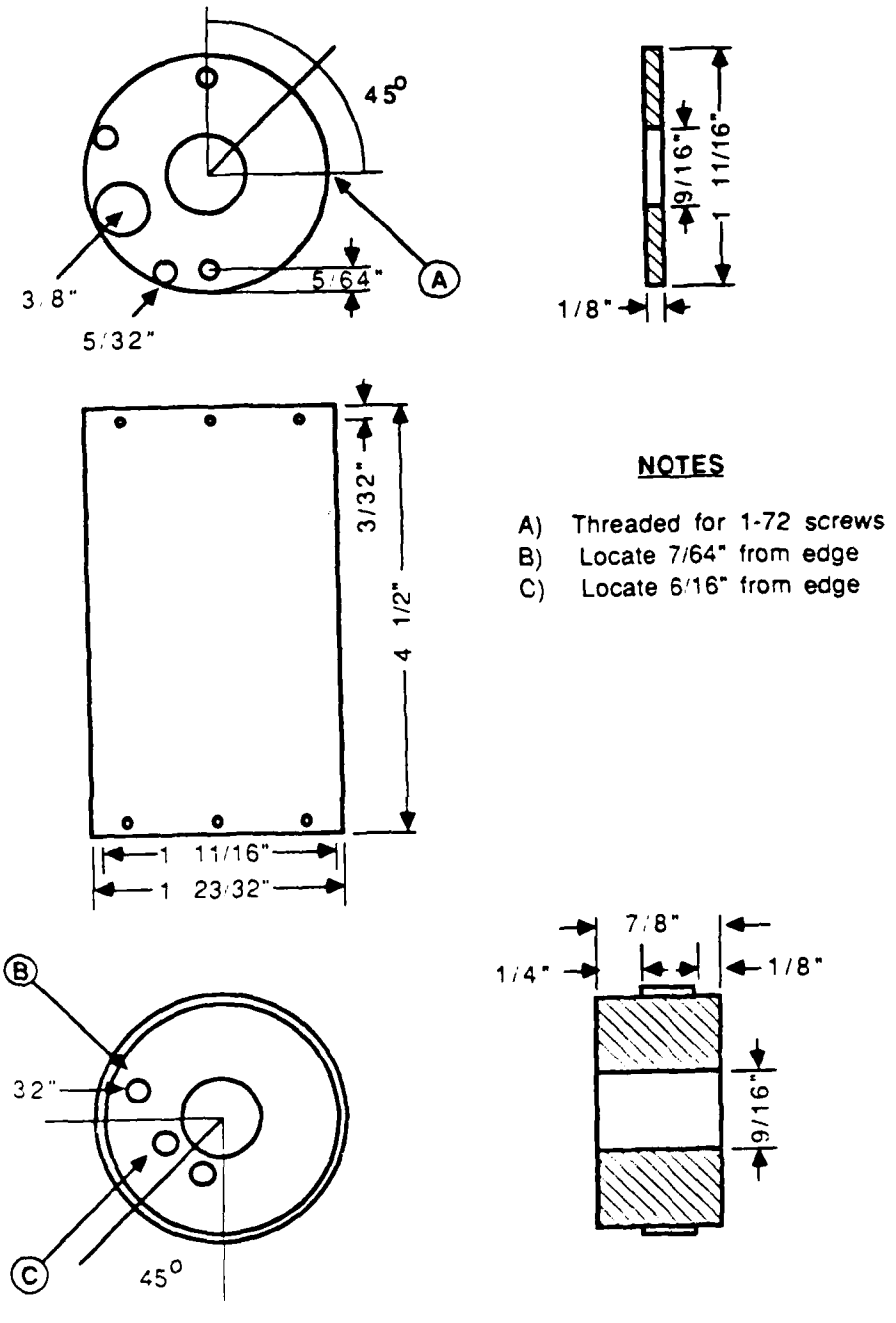


Figure 2.3
Pressure Vessel Insert



NOTES

A) Threaded for 1-72 screws
B) Locate 7/64" from edge
C) Locate 6/16" from edge

Figure 2.4
CSTR Dead Volume Insert

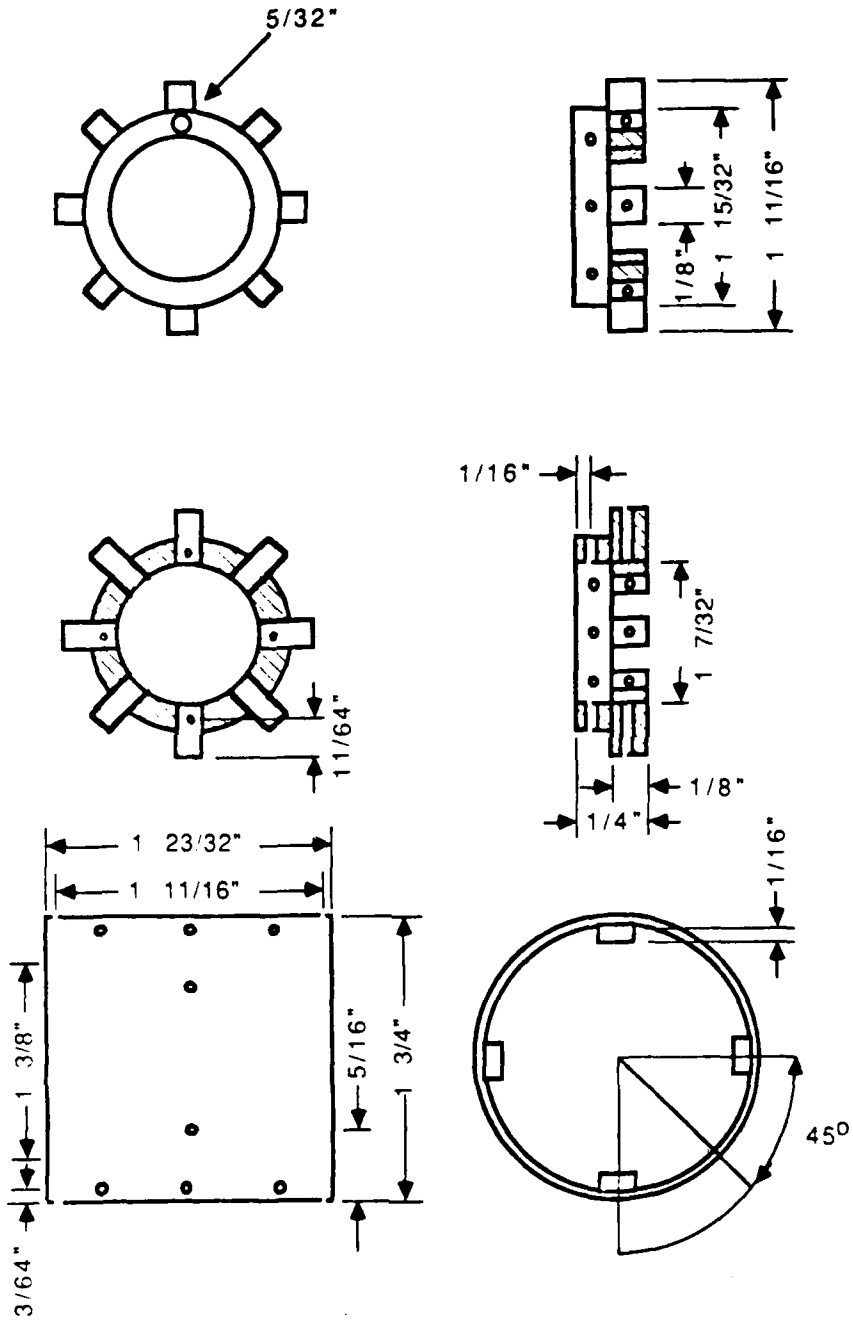


Figure 2.5
CSTR Catalyst Basket

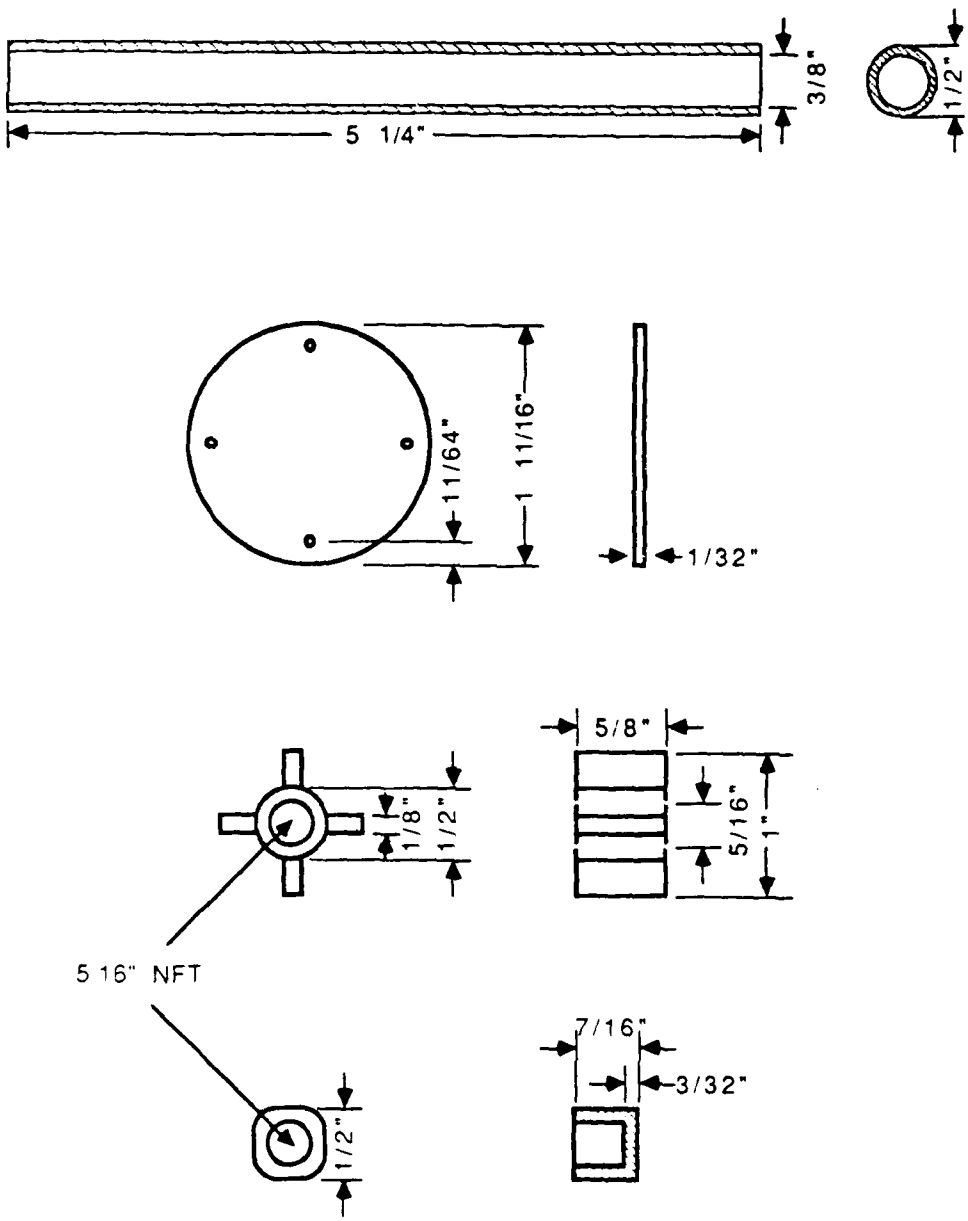


Figure 2.6
Impeller Shaft Sheath, Basket Bottom Plate
Impeller, and Impeller Lock Nut

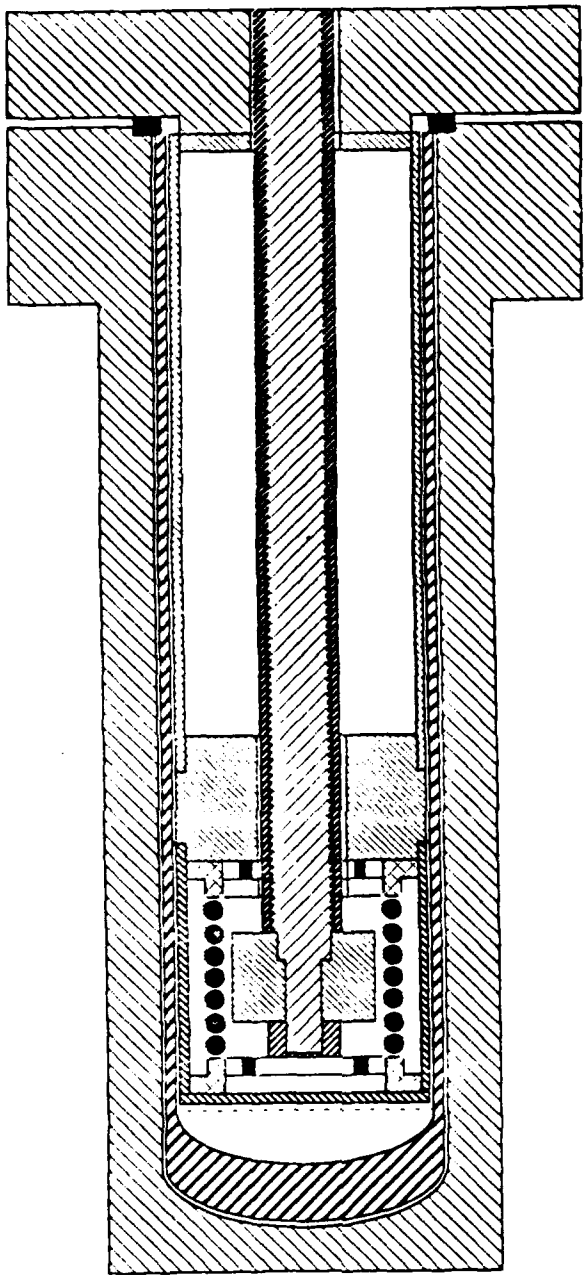


Figure 2.7
Assembled Reactor

Syringe Pump, two gas mixing chambers, and an iron carbonyl removal trap. A schematic of the system can be seen in Figure 2.8.

All gasses except water are metered by the MFCs. The Tylan controllers provide a very accurate measurement and control of the gases. The controller consists of a control valve, thermal sensors and the electronic circuitry required for the signals from an outside readout box. The controllers operate on the principal of temperature change as a gas flows through the meter. This temperature change is measured by two sensors, one at the inlet and the other at the outlet. The measured temperature difference is transformed into an electrical output signal which ranges from 0 to 5 volts dc. The circuitry of the meter creates a linear signal over the range of flow for a particular gas. In this case the range is from 0 to 200 standard cubic centimeters per minute (sccm). Each MFC can be used for any gas or mixture of gases by consulting the table of conversion factors provided in the Mass Flow Instructions Manual [21]. For these studies the MFCs were calibrated using a bubble meter. The calibration curves can be seen in Appendix A.1.

Water, in the form of steam, was injected into the system using a Sage Instruments Model 220 Syringe Pump and a water evaporating column (Figure 2.9). The water evaporating column was operated at 105°C and 1 atmosphere. The injection rate of water (at 27°C, 1 atm) needed to produce a specified amount of steam at standard conditions (0°C, 1 atm) was calculatied from the calibration curve shown in Appendix A.2.

After metering, the gases passed through check valves and Solenoid Shut Off Valves (SSOV). The check valves were placed after the MFCs to protect them from damage due to back flow in the system. The SSOVs were placed to allow computer control of the gas flow through the data output card (DOT), and to stop all gas flow in the event on an electrical outage.

Carbon monoxide, methane, carbon dioxide, and nitrogen were mixed and then passed through a heated chamber containing 5 Angstrom pore size molecular sieve adsorbent, to remove any traces of iron carbonyl present in the carbon monoxide feed gas.

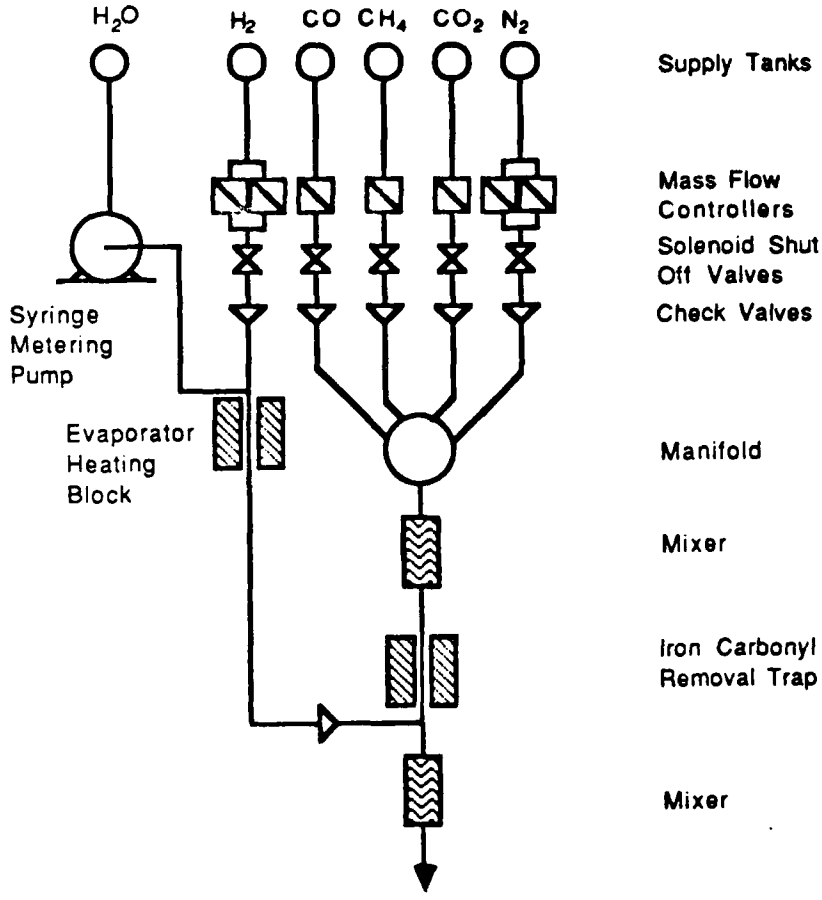


Figure 2.8
Gas Metering and Mixing

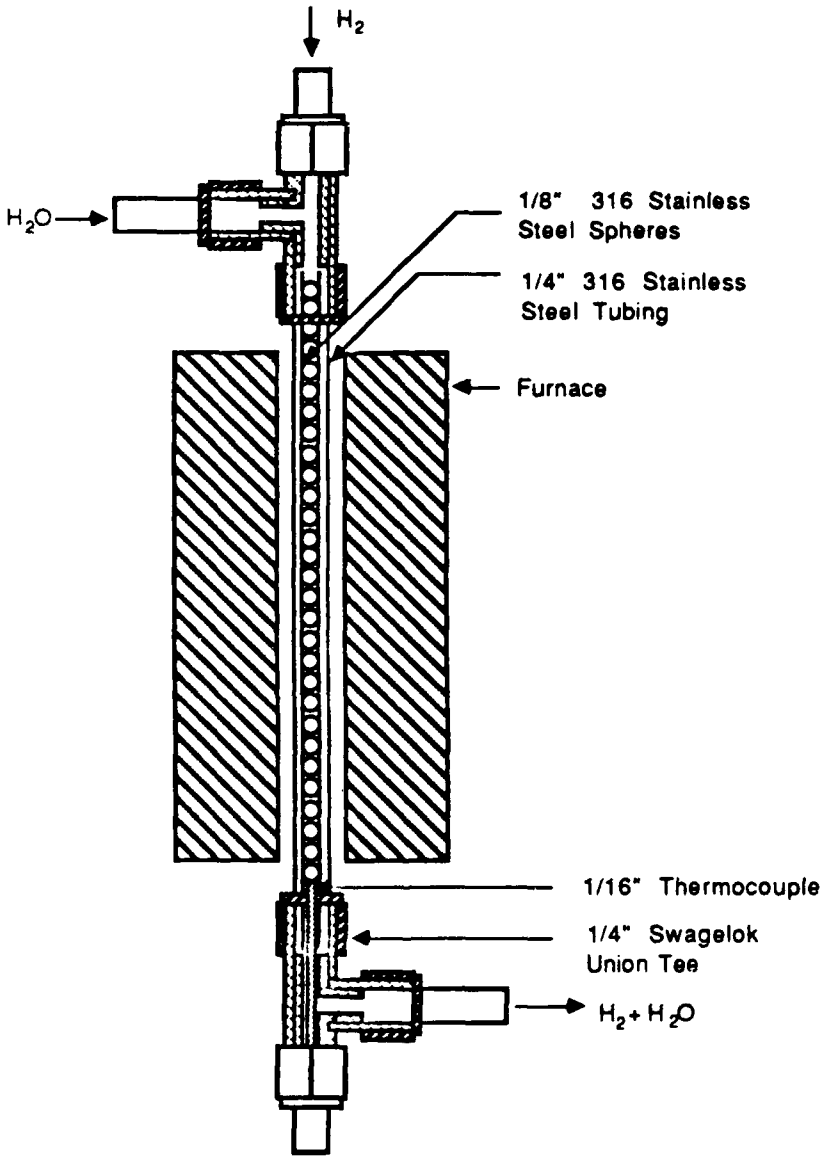


Figure 2.9
Water Evaporating Column

Iron carbonyl forms from a reaction of carbon monoxide with iron at high pressure, such as encountered in pressurized gas cylinders. As discovered in the early stages of this research, iron carbonyl leads to deactivation of methanation catalysts. To remove the iron carbonyl from the feed gas, two measures were taken. First, aluminum cylinders were used to supply carbon monoxide. This reduced effectively the amount of iron carbonyl present in the feed but did not eliminate a small amount produced in bulk storage. Secondly, the molecular sieve trap was installed. As pointed out by Schay et al. [22], iron carbonyl is decomposed on Cab-O-Sil and other adsorbents at about 125°C. The trap proved to be successful. Magnetic analysis of the molecular sieve adsorbent showed that iron was deposited on the surfaces [23].

Hydrogen was passed through the evaporating column to acquire a desired vapor pressure of steam. Steam and hydrogen then joined the other reactant gases in a second mixer, followed by a stream splitter. One branch flowed to a preheater followed by the reactor, while the other passed to the chromatograph for analysis of the feed composition.

All tubing after the water evaporating column and after the iron carbonyl trap were made of copper and were heated with electrical heating tapes. Copper was used to prevent coke formation on the tube walls. The heating tapes prevented steam from condensing.

2.3 Process Flow

The process flow diagram is shown in Figure 2.10. The original three reactor system, designed by Torres-Acosta[18],was replaced with a single CSTR. Existing reactor furnaces were modified to serve different functions. One was used for the water evaporation column, the other for a preheater. MFCs, SSOVs, and check valves previously used for controlling reactor feed flow were allocated different duties, two on the hydrogen and nitrogen feed lines to increase the maximum system flow from 200 sccm to

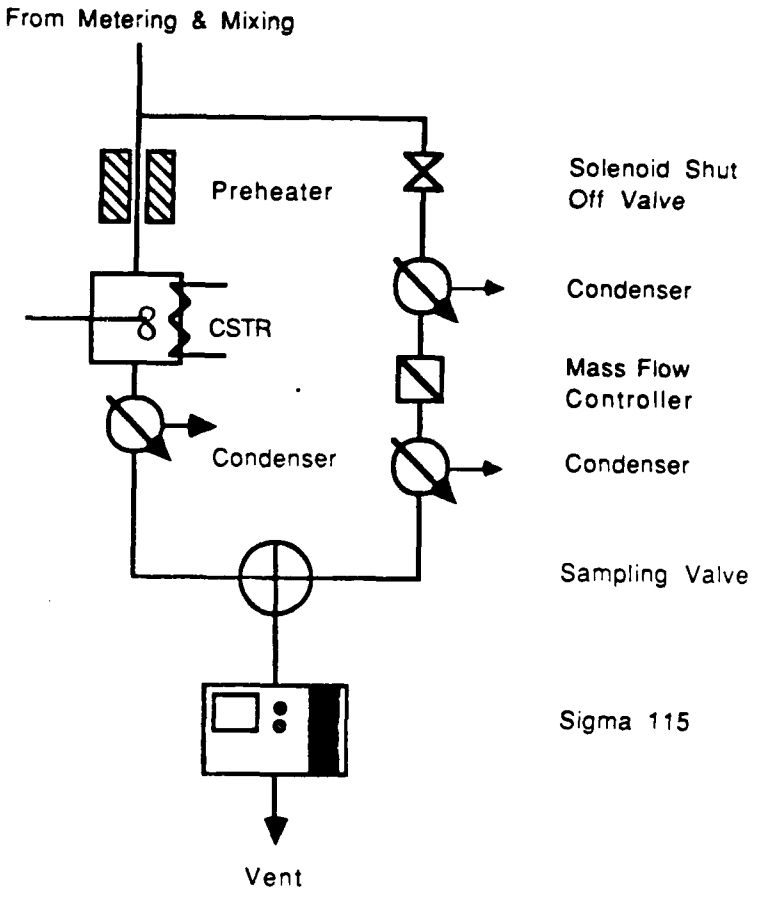


Figure 2.10
Process Flow

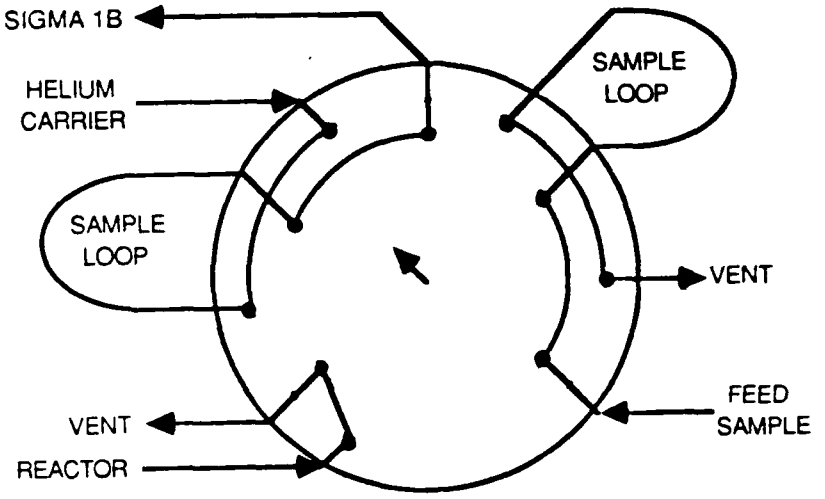
400 sccm, and the third on the feed sample line to give an accurate measurement of the feed sample rate. This replaced the needle valve previously used.

Upon leaving the second mixer, the gas stream was split. One stream went to the gas chromatogragh (GC) for analysis, while the other went to the reactor. The feed gas sample stream passed through a check valve and a condenser before reaching the MFC. It was important to remove all water before the gas passed through the MFC and the GC. Condensing water tends to plug the MFC sensor ports, change the size of the feed sampling loop, and disrupt the accurate analysis of the feed gas by the Thermal Conductivity Detector (TCD) of the GC. The sample then passed through a SSOV to the MFC so that the exact amount of gas leaving the system was known. This increased the accuracy of the material balances performed on the system.

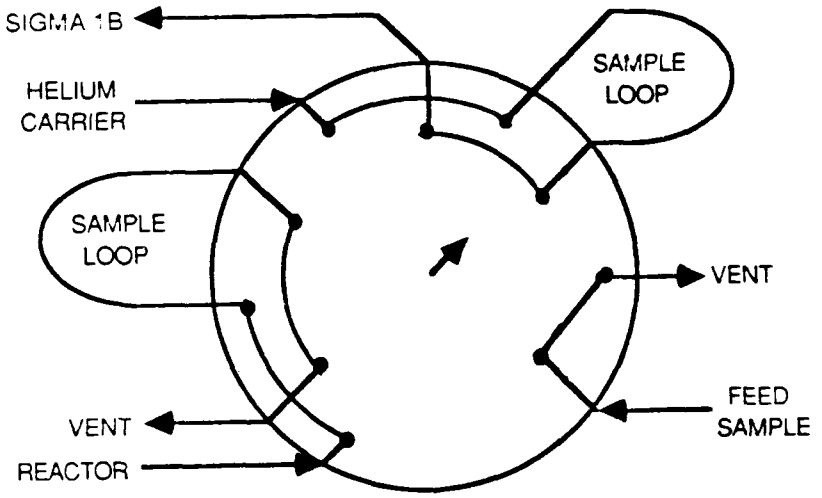
The reactor feed stream passed through a preheater consisting of a copper tube packed with alumina. The gas, now at reaction temperature, next passed to the CSTR. The product stream was carried by copper tubing to the condenser, where all of the water was removed before analysis of the product stream by the GC. Here again, the water must be removed to insure accurate analysis of the product stream. Analysis of the water content of either the feed or product stream is not critical. Since the exact feed concentration is known, a carbon balance allows for the calculation of the amount of water in the product stream. This is explained in Chapter 4.

2.4 Gas Sampling

On-line gas sampling was accomplished with one Valco Ten-Port Valve [24], fitted with an air actuator (Figure 2.11). The complex sampling system used by Torres-Acosta [18] was no longer needed because there was only one reactor product stream, one feed



Position A: Inject Reactor Sample



Position B: Inject Feed Sample

Figure 2.11
Valco Ten-Port Valve

sample stream, and one GC. This allowed the feed and product streams to be sampled alternately.

2.5 Product Analysis

On-line feed and product analysis was conducted by a Perkin Elmer Sigma 1B Analyzer equipped with a thermal conductivity detector (TCD). The sigma 1B Analyzer was interfaced with a Sigma 115 Console with Level 2 communications [25].

The Sigma 115 console is the key to the exact analysis of the feed and product samples. The console receives the voltage signals from the TCD of the Sigma 1B, translates them to component peak areas, manipulates the data using a prescribed method, and prints a report. The console has the ability to receive signals from two analyzers simultaneously, control the physical conditions within each analyzer independently, analyze data, and print reports for each analyzer.

The console uses a generated method [26] which controls physical conditions within each analyzer, collects data over prescribed times, and analyzes data using different analytical techniques specified by the user. The method used for the entire project is listed in Appendix B. The response factors listed were obtained using the calibration routine outlined in the Perkin Elmer Sigma 115 User Manual [27].

The sigma 1B analyzer was equipped with two matched Supleco, 15 foot, Carboseive B columns. The columns were designed to give good separation of low molecular weight molecules.

A 9% hydrogen in helium carrier gas was used in the study. This mixture was recommended by Purcell and Ettre [28] to obtain a more linear, and thus more accurate, analysis of hydrogen. Such a carrier mixture was not used by either Torres-Acosta [18] or Cullinane [15].

The TCD of the Sigma 1B measures the concentrations of gases in a mixture by comparing the thermal conductivity of the sample mixture, with the thermal conductivity of the pure carrier. As the gas sample is carried through the Carboseive B GC columns, the individual components of the mixture are adsorbed on the Carboseive B and released individually at a certain rate, which is dependent upon the temperature of the columns. This causes the individual components to elute at different times, thus the TCD can detect the amount of a certain component by comparison with the pure carrier gas. Components with a thermal conductivity higher than that of the carrier give a positive signal, those with a lower thermal conductivity a negative signal.

The thermal conductivity of hydrogen is slightly smaller than that of helium because hydrogen has a lower molecular weight. Similarly, components with a higher molecular weight than helium produce a positive signal. As pointed out by Purcell and Ettre [28], if the amount of hydrogen in the sample is below 8%, a positive signal results that is very nonlinear with hydrogen concentration. If the amount of hydrogen in the sample is above 8%, a negative signal results which is linear with hydrogen concentration. Thus using 9% hydrogen in the helium carrier gas gives a negative linear signal for hydrogen. The negative signal was inverted and treated as a positive signal in the analysis of the sample composition.

2.6 Process Control

In this section a brief description of the process control system is given, but for a more detailed description the work of Torres-Acosta [18] and Cullinane [15] should be consulted.

The heart of the process control system (Figure 2.12) is an Analog Devices MACSYM 2 (Measurement and control System) process control computer. The MACSYM

2 uses a form of the Basic Programming Language called MACBASIC. MACBASIC allows the use of English language type commands to create control algorithms. Through the use of MACBASIC, the MACSYM 2 was capable of real time operation and multitasking [29].

Through a series of ADIO (Analog/Digital/Input/Output) cards, the MACSYM 2 is able to communicate with the rest of the system. These cards are the analog to digital and digital to analog interfaces needed for various control and data acquisition tasks.

There are several ADIO cards in service in the MACSYM 2. The interrupt card (INT01) senses when the Sigma 1B analyzer is ready for a sample to be injected. The analog output card (AOC04) provides an analog signal to the temperature controllers. The analog input card (AIM03) reads the temperatures at various locations in the system. The digital output card (DOT) produces an electrical signal which activates a bank of relays which in turn activate the SSOVs. Tables 2.1 to 2.4 give the configuration of these cards. The process control program used for these experiments is listed in Appendix E.1.

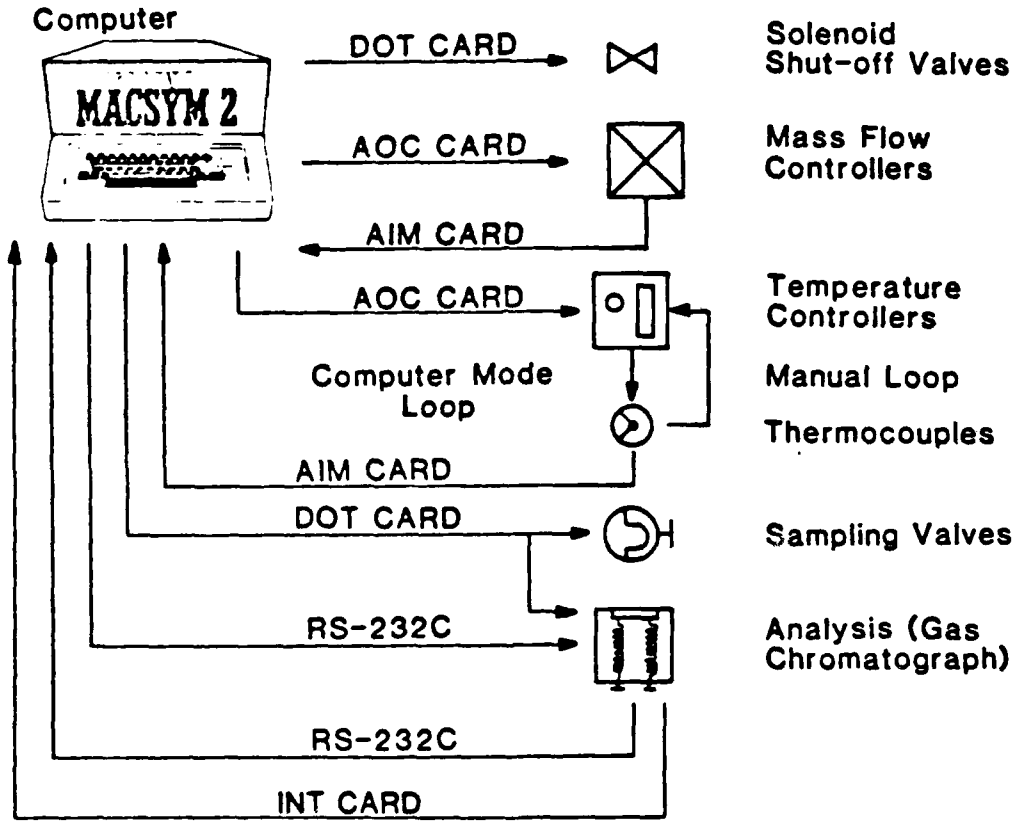


Figure 2.12
Process Control System Layout [18]

Table 2.1

ADIO Card Addresses
AOC Card: Slot 2

Channel	Controller
0	Iron Carbonyl Trap
1	Water Evaporator Column
2	Preheater
3	Reactor

Table 2.2

ADIO Card Addresses
INT Card: Slot 7

Channel	Event
0	GC1 Ready Light
1	Unused
⇓	⇓
7	Unused

Table 2.3

ADIO Card Addresses
AIM Card: Slot 0

Channel	Thermocouple
0	Unused
1	Reactor: Inlet
2	Unused
3	Unused
4	Water Evaporating Column
5	Iron Carbonyl Trap
6	Reactor: Catalyst Bed
7	Unused
8	Preheater
9	Unused
10	Unused
11	Unused
12	Reactor: Gas
13	Unused
14	Unused
15	Unused

Table 2.4

ADIO Card Addresses
DOT Card: Slot 5

Channel	Valve
0	N_2
1	CO_2
2	CO
3	CH_4
4	H_2
5	H_2 Aux.
6	N_2 Aux.
7	Feed Sample
8	Unused
9	Unused
10	Unused
11	Unused
12	Injection Position A
13	Injection Position B
14	Unused
15	Unused

CHAPTER 3

EXPERIMENTAL PROCEDURE

This section describes the experimental procedure used throughout the study. Covered in this chapter are the procedures used for calibration of the equipment, testing of the reactor, loading of the reactor, and measurements on the two catalysts studied.

3.1 Equipment Calibration

Proper calibration of the instruments was important to the accuracy and reproducibility of the experimental results. Because of this fact the calibration of the instruments was checked at the beginning of each series of experimental runs, approximately every three months.

The calibration of the mass flow controllers (MFC) was done with a bubble meter at the exit side of the MFC. The digital read-out was varied over the range of the meter (0 to 200 sccm) and the flow rates measured with the bubble meter. Measured flow rates were then converted to standard conditions (0°C, 1 atm). The assumption of an ideal gas was reasonable because the gases were at atmospheric pressure and 23°C. The ideal gas law gave a correction factor of 0.92 to convert the measured volumetric flow rate in cubic centimeters per minute to standard cubic centimeters per minute (sccm). Calibration curves were then plotted comparing digital read-out and flow in sccm (Appendix A.1). These calibration curves eliminated the need for mechanical adjustments to the MFCs, as done by Torres-Acosta [18], thus making the calibration procedure faster and more reliable.

The syringe pump was calibrated in a similar manner. The digital read-out was varied over the range of the pump (0 to 1000) and deionized water collected over a thirty minute period for each setting. The water was then weighed and the volumetric flow rate

determined. From the operation conditions of the water evaporation column (105°C, 1 atm), the rate of steam production in sccm could be determined. The calculations and calibration curve are shown in Appendix A.2.

Calibration of the Sigma 115 Gas Chromatograph (GC) was done following the general instructions given in the Sigma 115 Console Instructions manual [26]. Before calibration, the Carboseive B columns of the Sigma 1B analyzer were conditioned by heating them to 195°C for eight hours while passing carrier gas through them. The columns were then cooled to the operating temperature with the carrier gas flowing. After conditioning the columns, an optimized operating temperature for the analyzer oven was then determined. The temperature must be high enough to allow the sample to pass quickly through the GC columns, yet low enough for a good separation of individual component peaks. An optimum temperature was found by using an equimolar mixture of the gases as a sample, and adjusting the temperature so that all peaks could be read distinctly. The relative retention times of the various components were then determined by choosing one component (carbon monoxide) as a reference.

In order for the Sigma 115 Console to compute the concentrations of the components of the gas mixture, relative response factors must be determined. First, equal volume samples of the pure gases were analyzed by the GC and their peak areas determined. Secondly, all of the peak areas were divided by the peak area of the standard, carbon monoxide, to yield the relative response factors (Table 3.1).

The response factors and relative retention times were used to generate the operating method (Appendix B). The response factors were then tested by analyzing gas samples of known composition, thus fine tuning the factors to give more accurate results in the concentration ranges being studied. Response factors used during this study differ from those used by Torres-Acosta [18] and Cullinane [15] because of the different carrier gas.

Table 3.1

Response Factors and Retention Times
For Sigma 1B Analyzer

Component	Retention Time (Minutes)	Response Factor
Hydrogen	1.50	32.00
Nitrogen	2.68	0.498
Carbon monoxide	3.15	0.500
Methane	5.80	0.595
Carbon dioxide	12.5	0.426

The response factors of the GC method were recalculated each time a new cylinder of carrier gas was installed. This was done because the composition of the hydrogen / helium mixture changed slightly with each cylinder. Other than the response factors, all other parameters remained the same throughout the study.

3.2 Reactor Testing

Before the reactor could be used with confidence, it was necessary to determine whether it was a true CSTR and if the metal was catalytically inert. The reactor was thoroughly cleaned with acetone to remove any oils or other foreign materials left during construction. It was assembled and heated to 500°C in the presence of nitrogen for twenty-four hours to vaporize any residual oils or other contaminants, then cooled to room temperature in nitrogen.

To determine whether the reactor was catalytically inert, it was loaded with 1/8" alumina pellets and operated in the temperature range of 300 to 500°C with an equimolar feed of carbon monoxide, carbon dioxide, methane, nitrogen, and hydrogen. Analysis

showed the same composition for feed and product streams, thus proving that the reactor metal and the alumina pellets are catalytically inert.

The reactor design had been thoroughly tested by Hadjigeorghiou [17] who found it to be a true CSTR. To confirm this the following mixing test was performed. After loading the reactor with a full charge of catalyst (225 pellets), the temperature was increased to 400°C, the catalyst reduced for four hours in hydrogen, and the feed mixture composed of 10% carbon monoxide, 20% hydrogen, and 70% nitrogen started. The impeller speed was varied from 0 to 2000 RPM. For the 0.5% rhodium catalyst, no variation in conversion was noticed above an impeller speed of 750 rpm. The 70% nickel catalyst showed a drop in conversion at speeds below 1750 RPM. From these tests it was concluded that the reactor was perfectly mixed with the impeller speed at 2000 RPM. This had been shown earlier by Hadjigeorghiou [17]. Also, as noted by Hadjigeorghiou, there existed a small temperature difference between the catalyst bed and the gas phase in the reactor. Between temperatures of 300°C and 500°C, this temperature difference ranged from 13°C to 21°C. It was later found that part of this difference was caused by the thermocouples, which did not read the exact same temperature in the operating range of the reactor. No other tests, such as residence time analysis, ect. were needed, since Hadjigeorghiou had applied similar proceedures to confirm good mixing.

3.3 CSTR Loading

Loading the CSTR is one of the most critical steps in the experimental procedure. Improper handling can lead to irreparable damage to the reactor. Table 3.2 outlines the steps required to properly assemble and disassemble the CSTR.

Table 3.2

Assembly / Disassembly Procedure

ASSEMBLY

a) Check all screws for tightness and inspect reactor parts for cracks and contaminants.

b) Inspect all tubing fittings for tightness and cracks.

c) With the bottom of the basket removed, drop catalyst pellets and alumina pellets between the retaining screens. DO NOT force the pellets. Be certain to disperse the catalyst pellets with alumina for good heat dispersion.

d) Place the catalyst retaining ring in the basket. DO NOT force it into place.

e) Place the basket horizontally on a table with the thermocouple hole at the top and shake the basket horizontally to settle the pellets away from the thermocouple entrance.

f) Place the basket on the machined end of the dead volume insert, being certain that the screen does not get bent when the thermocouple enters the basket. If the screen is bent the basket must be emptied and the screen straightened. If this is not done the screen will be caught in the impeller and the basket and thermocouples will be destroyed.

g) Place the bottom on the basket and secure it with screws.

h) While firmly grasping the magnetic drive unit and guiding the basket with your other hand, lift the unit so it is vertical.

i) Place the reactor assembly in the pressure vessel. Be certain to keep the unit vertical while doing this or the dead volume insert may be bent or cracked. The reactor parts are ONLY 1/32" thick.

j) Install the pressure vessel bolts and tighten opposite bolts sequentially.

k) Connect the inlet line, cooling water lines, and thermocouple leads.

l) Pressure test the system to check for leaks.

DISASSEMBLY

a) Cool the reactor in nitrogen from its reaction temperature especially when working with nickel catalysts to remove any traces of nickel carbonyl.

b) Follow the Assembly instructions in reverse order.

c) Place the magnetic drive unit in the wooden stand

3.4 Catalyst Testing

The catalyst testing facility is almost completely automated, except for the MFCs which were set manually. For these studies the MACSYM 2 was used only to operate the sampling valves and record temperatures from different parts of the unit (Appendix E.1). The large lag-time in the reactor temperature control loop made it impractical to control the reactor temperature with the computer. As a result, experiments were arranged so that one temperature was studied over a series of feed component partial pressures, each set manually. This method of data acquisition saved time because the reactor would stabilize at a steady state five times faster after a change in feed composition, than it would after a change in temperature setpoint.

To obtain good kinetic data, the CSTR was operated so the conversion within the reactor was very small, or differential. Operating at this low level of conversion (under 10%) allows the methanation reaction to dominate and suppresses the shift reaction. This was important because the kinetics of the methanation reaction were of interest.

The testing procedures for the 0.5% Rh catalyst and the 70% Ni catalyst are similar, yet different enough to describe them separately.

The 0.5% Rh catalyst was to be tested between 300°C and 500°C at 50°C increments. Since this catalyst was to be used in the first of a series of methanators, it was desirable to test it and obtain kinetic data with and without steam in the feed stream. The series of experimental runs are outlined in Tables 3.3 and 3.4.

Table 3.3

0.5% Rhodium Catalyst
Study Without Steam

Run Number	H_2 to CO Ratio	Flow Rate H_2 (sccm)	FlowRate CO (sccm)	Flow Rate N_2 (sccm)
1	2.0	200	100	100
2	1.5	150	100	150
3	1.0	100	100	200
4	2.0	160	80	160
5	1.5	120	80	200
6	1.0	80	80	240
7	2.0	120	60	220
8	1.5	90	60	250
9	1.0	60	60	280
10	2.0	240	120	40
11	1.5	180	120	100
12	1.0	120	120	160
13	1.5	210	140	50
14	1.0	140	140	120
15	1.5	234	156	10
16	1.0	156	156	88
17	1.0	176	176	48
18	1.0	196	196	8
19	2.0	80	40	280
20	1.5	60	40	300
21	1.0	40	40	320
22	2.0	40	20	340
23	1.5	30	20	350
24	1.0	20	20	360

After the CSTR was loaded, following the instructions in Table 3.2, it was purged with nitrogen at 100 sccm for 20 minutes. All of the system furnaces were turned on and the CSTR heated at a rate of 3°C per minute with hydrogen flowing at 50 sccm. At 10°C below the desired operating condition, the reactant gas flow for a selected standard condition was started. The total gas flow for all experimental runs was 400 sccm. The CSTR attained steady state after 15 minutes and the standard condition was run for four product samples. After the fourth sample, the feed composition was changed. The new condition was run until four product samples were taken, then the composition changed

again. This process continued for three composition changes. Before the CSTR was shut down, after the completion of several runs, the standard feed composition was measured again. This data was used to determine if the catalyst deactivated, and if so, by how much. This information was used to normalize the experimental data. After the standard run, all reactant gases were shut off except for nitrogen, which flowed at 100 sccm until the reactor and furnaces cooled to room temperature. Once cooled, the nitrogen flow was decreased to 20 sccm so that the catalyst remained in an inert environment until the next series of experiments.

Table 3.4

0.5% Rhodium Catalyst
Study With Steam

Run Number	H_2 to CO Ratio	Flow Rate H_2 (sccm)	Flow Rate CO (sccm)	Flow Rate H_20 (sccm)	Flow Rate N_2 (sccm)
1	2.0	160	80	80	80
2	1.5	120	80	80	120
3	1.0	80	80	80	160
4	2.0	120	60	60	160
5	1.5	90	60	60	190
6	1.0	60	60	60	220
7	2.0	184	92	92	32
8	1.5	150	100	100	50
9	1.0	100	100	100	100
10	1.0	120	120	120	40
11	1.0	130	130	130	10
12	2.0	40	20	20	320
13	1.5	30	20	20	330
14	1.0	20	20	20	340
15	2.0	80	40	40	240
16	1.5	60	40	40	260
17	1.0	40	40	40	280

The 70% Ni catalyst was tested between 300°C and 500°C at 50°C increments. This catalyst was to be used in the last methanator as a clean-up catalyst, and thus it was tested with steam in the feed stream. Nickel catalysts coke extensively at hydrogen to

carbon monoxide ratios lower than three. It was expected that the steam in the feed would reduce the coking so that good experimental data could be obtained. The series of experimental runs are outlined in Table 3.5.

Table 3.5

70% Nickel Catalyst
Study With Steam

Run Number	H_2 to CO Ratio	Flow Rate H_2 (sccm)	Flow Rate CO (sccm)	Flow Rate H_20 (sccm)	Flow Rate N_2 (sccm)
1	2.0	160	80	80	80
2	1.5	120	80	80	120
3	1.0	80	80	80	160
4	2.0	120	60	60	160
5	1.5	90	60	60	190
6	1.0	60	60	60	220
7	2.0	184	92	92	32
8	1.5	150	100	100	50
9	1.0	100	100	100	100
10	1.0	120	120	120	40
11	1.0	130	130	130	10
12	2.0	40	20	20	320
13	1.5	30	20	20	330
14	1.0	20	20	20	340
15	2.0	80	40	40	240
16	1.5	60	40	40	260
17	1.0	40	40	40	280

The daily operating procedure for the 70% Ni catalyst was the same as that for the 0.5% Rh catalyst except for one initial procedure. Before a new catalyst charge could be used it had to be reduced to remove the small surface oxidation layer which the manufacturer added for passivation purposes. The 0.5% Rh was not easily oxidized, and heating to reaction temperature in hydrogen was sufficient enough to remove any oxides. The 70% Ni catalyst was reduced by heating to 400°C with a hydrogen flow of 50 sccm and holding it at 400°C for eight hours. After this period of time, the catalyst could be

either held in the reactor in nitrogen for future experiments, or used directly by adjusting the reactor temperature to the desired reaction temperature.

To be certain the derived kinetic expressions accurately predicted the methanation and shift kinetics over a broad range of operating conditions, data was needed at high carbon monoxide conversions. For both the 0.5% Rh and 70% Ni catalysts several experimental runs were done at each temperature, where the conversion of carbon monoxide exceeded 30%, but was less than 70% to avoid equilibrium. The higher conversions were achieved by increasing the catalyst loading and repeating several of the runs outlined in Tables 3.3 to 3.5.

In addition to the kinetics, the durability of both catalysts had to be determined. One lifetime study, of 100 hours duration, was performed at 400°C on the 0.5% Rh catalyst. Lifetime studies of 300 hours duration at 300°C, 350°C, and 400°C were made on the 70% Ni catalyst. All lifetime studies were conducted with low H_2/CO ratio feeds and high carbon monoxide conversion.

CHAPTER 4

RESULTS AND DISCUSSION - 0.5% Rh

This chapter discusses the experimental results on the 0.5% Rh catalyst. In this chapter the experimental procedure is reviewed and any deviations or difficulties included. The methods of data analysis, the results without steam, the results with steam, the kinetics expressions, and the results of the lifetime study are presented and discussed.

4.1 Review of Experimental Procedure

The experimental procedure for the testing of the 0.5% Rh catalyst remained the same as described in Chapter 3 except the range of temperature was 400 to 500°C. This change was made because of the very low activity of the catalyst at temperatures below 400°C. Since the catalyst was not to be used at temperatures below 400°C, the acquisition of kinetic data in this range was not necessary.

The catalyst was reduced in hydrogen at 50 sccm while the reactor was heating to the operation temperature at a rate of 3°C $min.^{-1}$. At first this reduction period was not thought to be enough, so a different reduction method was tried. The catalyst was first heated in nitrogen to 400°C then reduced with hydrogen at 50 sccm for four hours. The activity was measured at a standard feed condition at 400°C. Another catalyst charge was then reduced by the original method and the activity measured at 400°C under the same feed condition. This test showed no difference in initial activity, so the original method was retained.

Maintenance to the system was minimal. All of the equipment operated well and did not fail. Every ten reactor loadings the Swagelok fittings connecting the reactor to the feed line had to be replaced. The fittings were damaged by a combination of heating-

cooling and assembly-disassembly cycles. Replacing these fittings reduced the danger of leaks. The wire screen of the catalyst basket was replaced every four months. Loading and unloading the basket caused the screen to distend out of shape, thus leading to fracture after several runs. The basket was replaced before it broke to prevent possible damage to the reactor during a run. Other routine maintenance included draining the water separators, and calibrating the instruments.

The only equipment modification made to the system after the initial reconfiguration was the addition of silica gel dryers after the water separators. These were necessary because the separators did not remove all of the water from the product stream, especially when water was added in the feed. Water in the analysis line to the GC changes the volume of the sample loops and produces a larger CO_2 peak during analysis, thus introducing inaccuracies.

4.2 Data Analysis

Manipulation of the data obtained from each experimental run was performed by an Apple Macintosh Plus computer, using the Basic programming language. All experimental data was entered via key board and stored in data files on floppy disks. Using the programs listed in Appendix E.2 & E.3, the data was stored, manipulated, and printed. These programs performed all of the material balances and calculated the rates of methanation. The data for all of the experimental runs for the 0.5% Rh catalyst are given in Appendix C.

4.2.1 Definitions

The results presented in Appendix C contain the following definitions. Conversion of CO is the moles of CO converted per mole of CO in the feed. The yield of methane is

moles of methane produced per moles of CO fed. The correction factor is the percent of original catalyst activity exhibited by the catalyst sample, during a particular run, taking 100% as the activity measured on new catalyst at a standard feed condition. A new standard activity was determined for each new catalyst loading, at a standard feed condition, for the temperature at which that loading was run. For example, if a series of runs were measured at 400°C, the standard activity was found at 400°C on the fresh catalyst at a standard feed condition. Each day the catalyst loading was reused, the standard feed condition was run both at the beginning of the day and at the end of the day. In this way the catalyst activity was known and any deactivation detected. Any deactivation which occurred over the course of a day was assumed to be linear. The mean of the deactivation over a certain run time was determined, and used to calculate the percentage of original activity in the catalyst sample. It should be noted that the data appearing in Appendix C was adjusted to account for any deactivation which occurred over an experimental run.

4.2.2 Sources of Deactivation

The formation and elimination of iron carbonyl from the reactor feed stream is discussed in Section 2.2. This cause of deactivation was detected at the start of the experimental work, and eliminated as a source of catalyst deactivation.

After the iron carbonyl poisoning problem was corrected, a contaminant in the catalyst support was suspected. The suspicion was justified by a magnetic measurement which revealed trace amounts of iron in the alumina support [30]. As pointed out by Mills [4], iron very strongly catalyzes the formation of carbon (Reactions {1.6} and {1.7}) and as shown in Figure 1.6, the formation of carbon is enhanced by the temperature and H_2/CO ratios used during the experimental runs. Despite this trace iron contamination, the catalyst was used, but strict attention to catalyst deactivation was necessary.

Carbon formation was observed at all temperatures studied. The carbon was very light and caused little fouling at temperatures above 400°C. Below 400°C the rate of carbon formation increased as temperature lowered. Formation of carbon, coupled with the catalyst's low activity at temperatures below 400°C, made the study of the kinetics in the 300 to 400°C range very difficult and was avoided.

After the completion of the experimentation on the 0.5% Rh catalyst, work by Patterson [31] revealed cata'yst sintering in the 400 to 500°C temperature range. In addition to the correction for deactivation, an additional correction was made to account for sintering. The rates at different temperatures were adjusted to the rhodium dispersion at 500°C by means of surface areas measured with dynamic hydrogen adsorption. These values are given in Table 4.1.

Table 4.1

Surface Areas of 0.5% Rh [16]

Temperature (°C)	Rhodium Surface Area m^2g^{-1} (Rh)
300	214
400	211
500	194
600	170

4.3 Results Without Steam in the Feed

The first series of experiments on the 0.5% Rh catalyst were conducted without steam in the feed. A series of experimental runs (Table 3.3) were made at 400°C, 450°C, and 500°C. Appendix C contains the tabulated results of these runs. In Figures 4.1 to 4.6

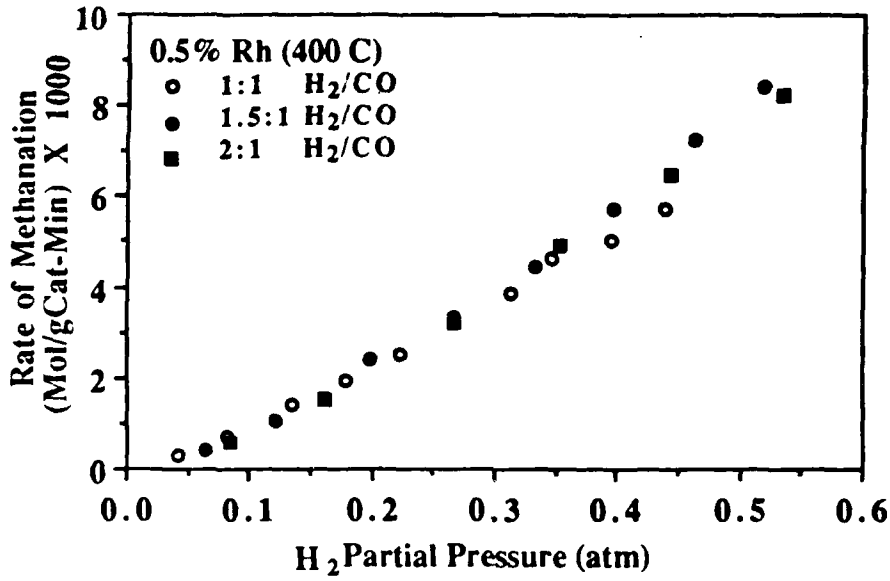


Figure 4.1
Methanation Rate versus H_2 Partial Pressure 400°C (No Steam in Feed)

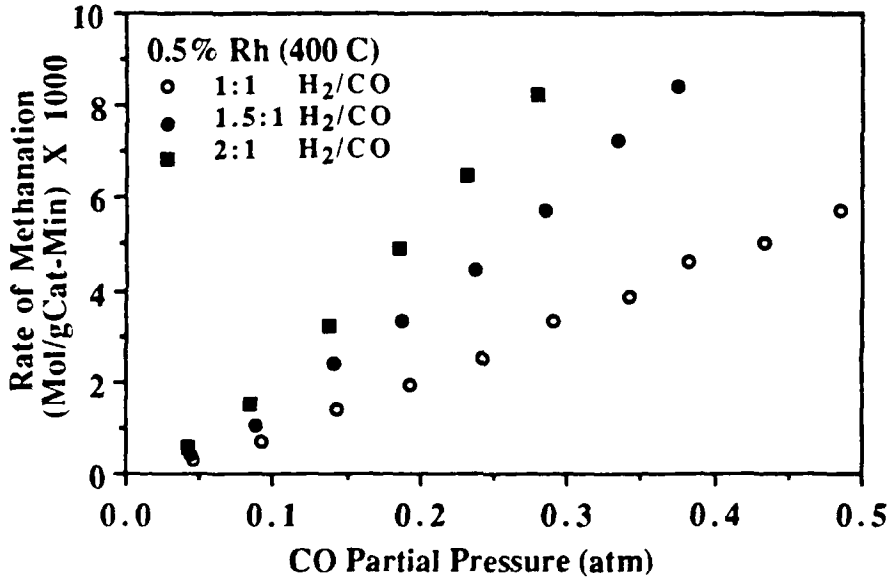


Figure 4.2
Methanation Rate versus CO Partial Pressure 400°C (No Steam in Feed)

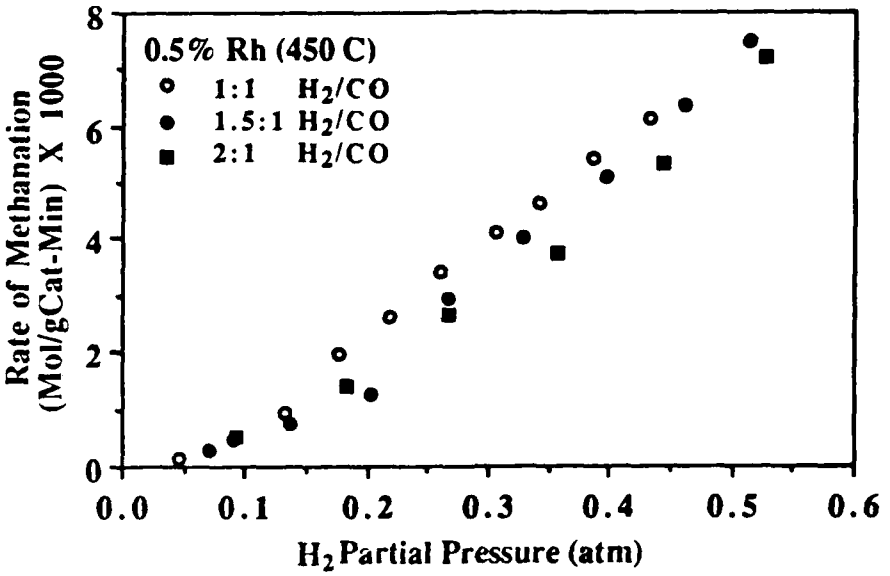


Figure 4.3
Methanation Rate versus H_2 Partial Pressure 450°C (No Steam in Feed)

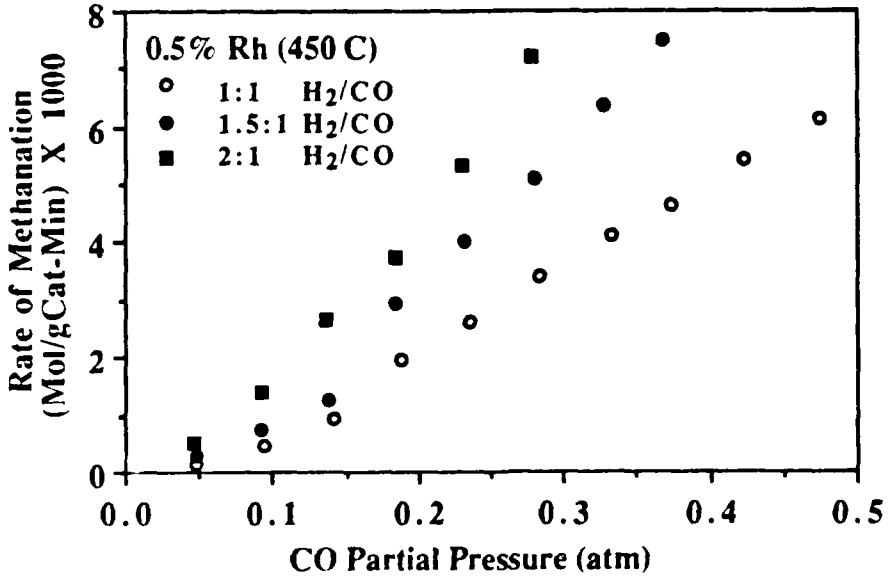


Figure 4.4
Methanation Rate versus CO Partial Pressure 450°C (No Steam in Feed)

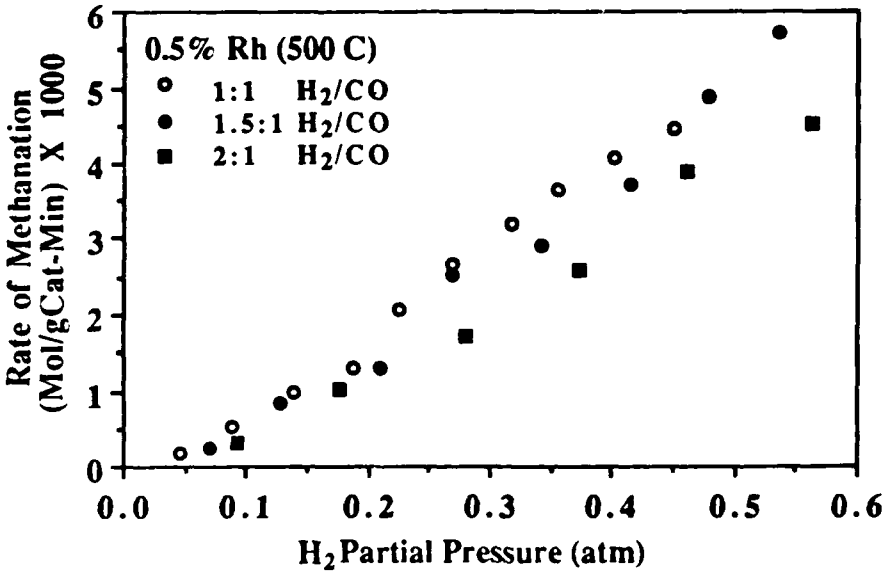


Figure 4.5
Methanation Rate versus H_2 Partial Pressure 500°C (No Steam in Feed)

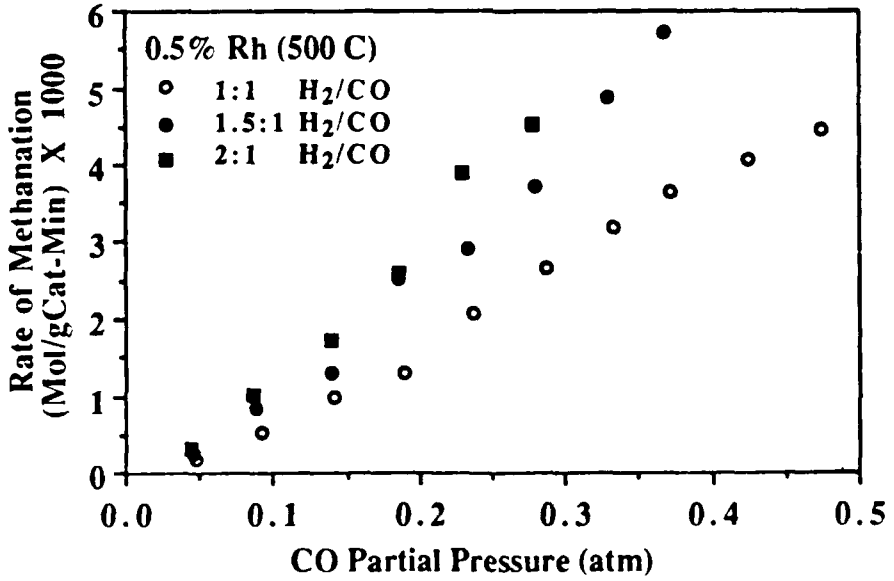


Figure 4.6
Methanation Rate versus CO Partial Pressure 500°C (No Steam in Feed)

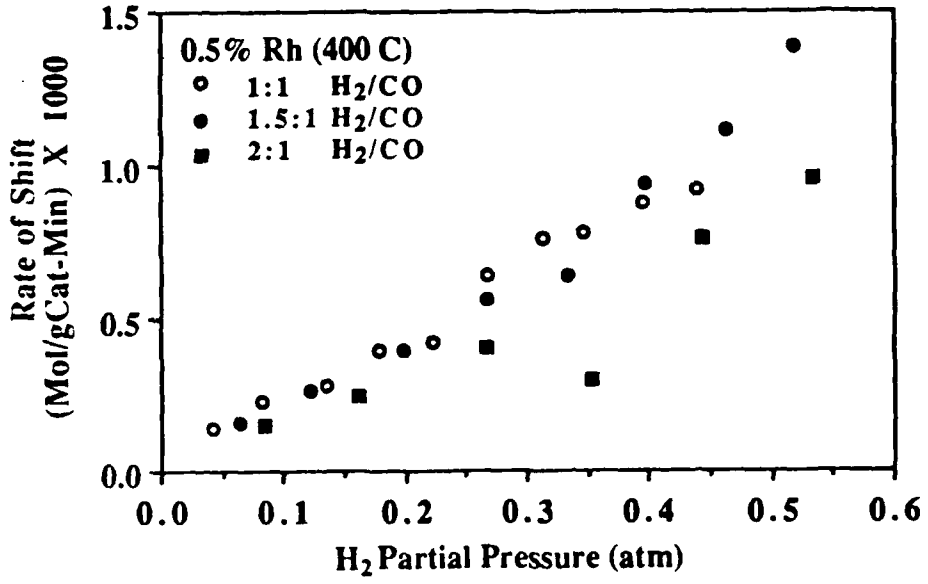


Figure 4.7
Shift Rate versus H_2 Partial Pressure 400°C (No Steam in Feed)

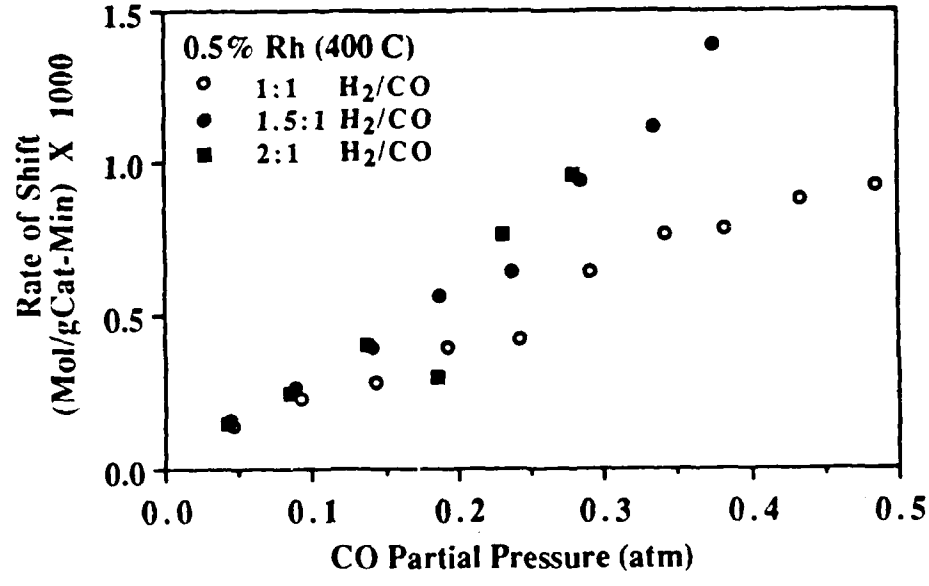


Figure 4.8
Shift Rate versus CO Partial Pressure 400°C (No Steam in Feed)

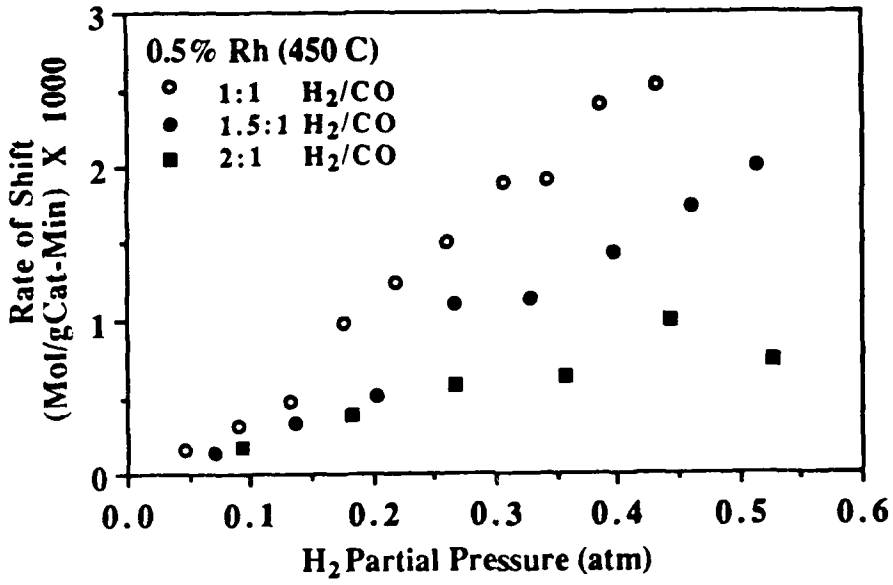


Figure 4.9
Shift Rate versus H_2 Partial Pressure 450°C (No Steam in Feed)

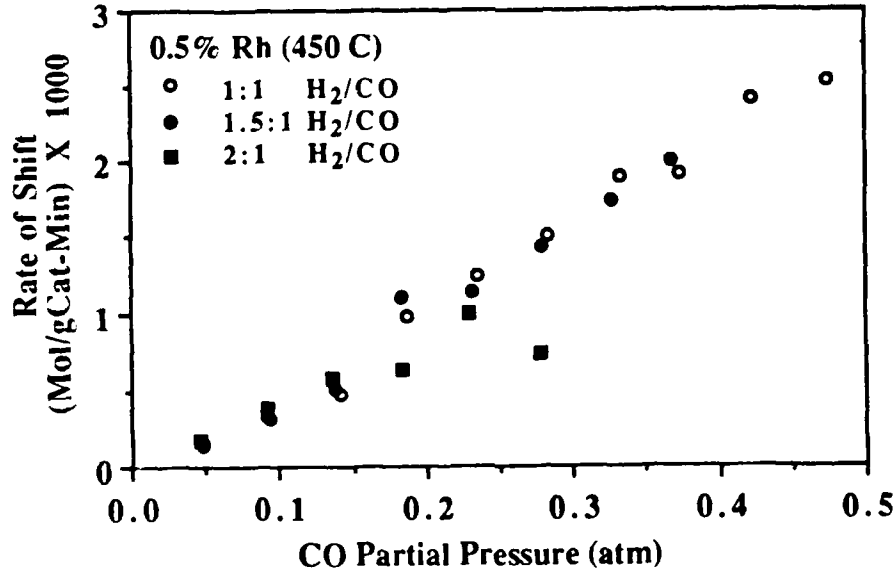


Figure 4.10
Shift Rate versus CO Partial Pressure 450°C (No Steam in Feed)

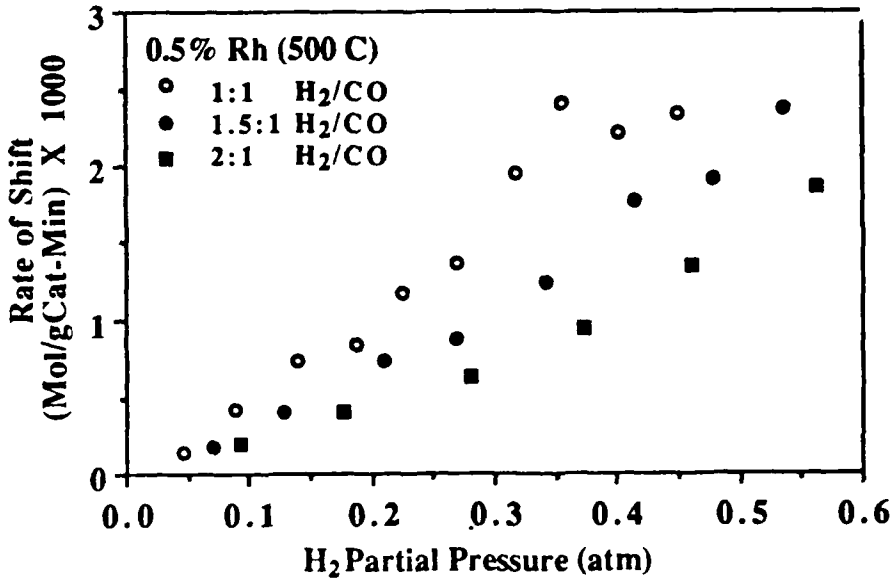


Figure 4.11
Shift Rate versus H_2 Partial Pressure 500°C (No Steam in Feed)

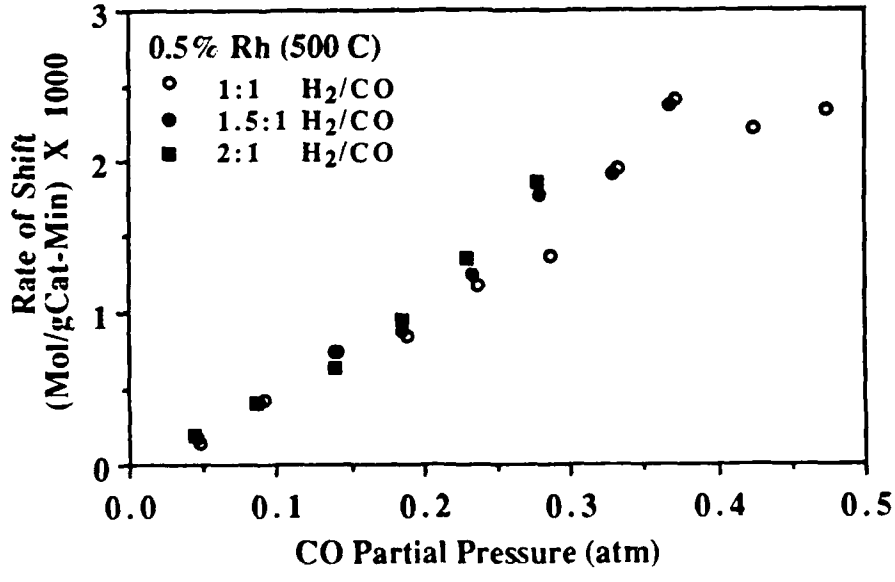


Figure 4.12
Shift Rate versus CO Partial Pressure 500°C (No Steam in Feed)

the rate of methanation is plotted as a function of H_2 and CO partial pressures. Figures 4.7 to 4.12 show the rate of shift.

From the plots of methanation rate versus partial pressure, one can see several trends. The rate of methanation has a near first-order dependence on the partial pressure of H_2. A similar first-order dependence can also be seen with the CO partial pressure, but with different curves for a different H_2/CO ratio, with 1:1 having the least slope and 2:1 the greatest. This feature shows the extent to which higher relative CO concentrations inhibit the formation of methane. Plots of shift rate versus CO partial pressure show a near first-order dependence, while plots versus H_2 partial pressure have a lot of scatter, caused by the different H_2/CO ratios, which leaves no observable trends.

4.4 Results With Steam in the Feed

The second set of experiments on the 0.5% Rh catalyst were made with steam in the feed at a 1:1 ratio with CO. A series of experimental runs (Table 3.4) were conducted at 400°C, 450°C, and 500°C. The tabulated results of these runs are in Appendix C. In Figures 4.13 to 4.18 the rate of methanation is plotted as a function of H_2 and CO partial pressures. Figures 4.19 to 4.24 show the rate of shift.

With steam in the reactor feed, the same trends observed without the steam were also observed. At this point a comparison can be made between the two sets of experimental runs. As seen in Figures 4.25 to 4.42 the addition of steam to the feed stream lowered the rate of methanation. This result is expected because water is a product of the methanation reaction.

$$3H_2 + CO \Leftrightarrow CH_4 + H_2O \qquad \{1.10\}$$

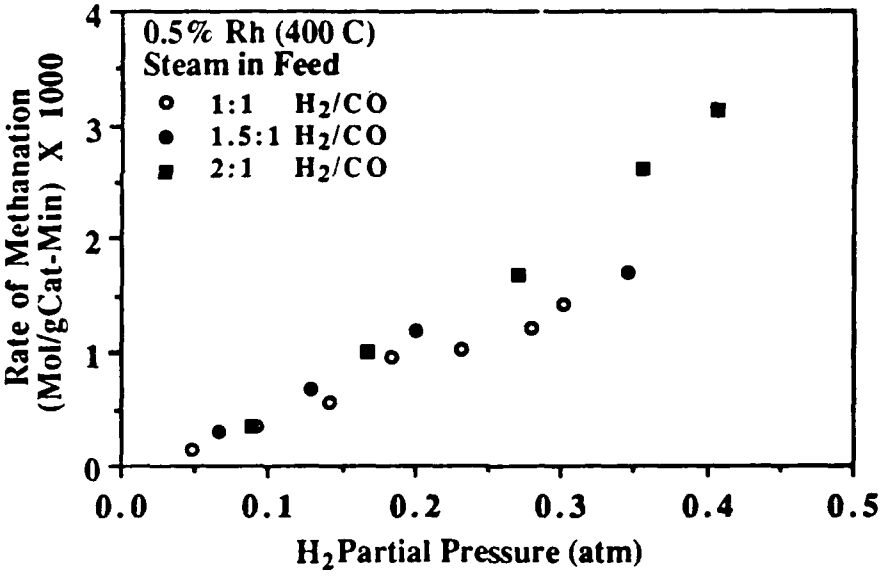


Figure 4.13
Methanation Rate versus H_2 Partial Pressure 400°C (Steam in Feed)

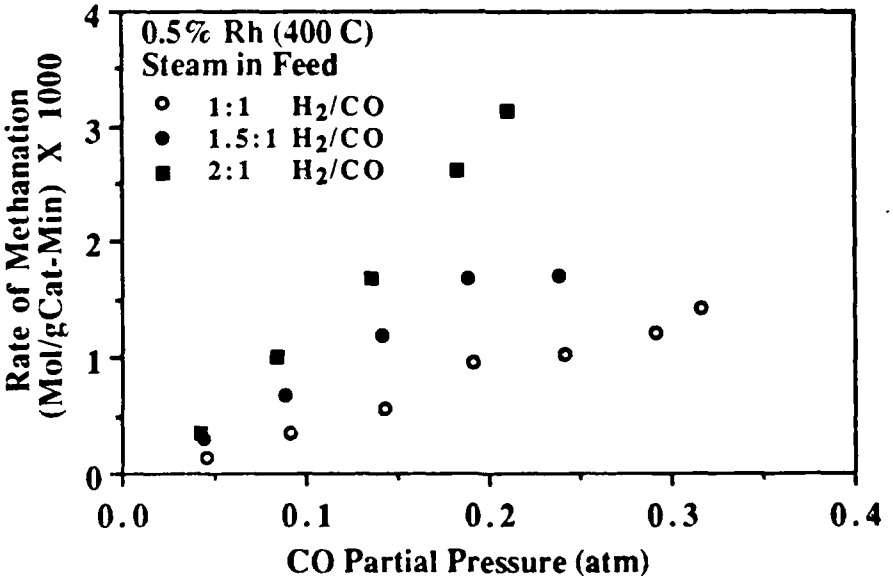


Figure 4.14
Methanation Rate versus CO Partial Pressure 400°C (Steam in Feed)

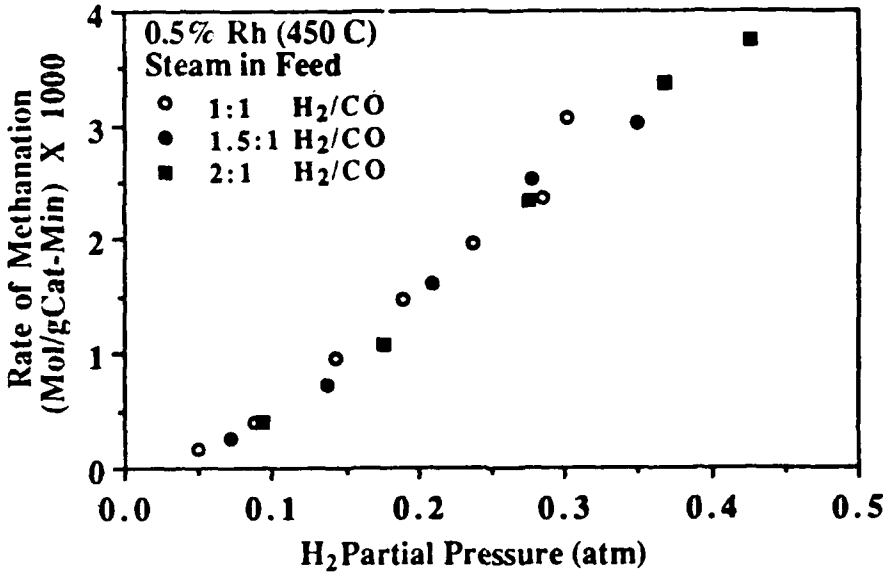


Figure 4.15
Methanation Rate versus H_2 Partial Pressure 450°C (Steam in Feed)

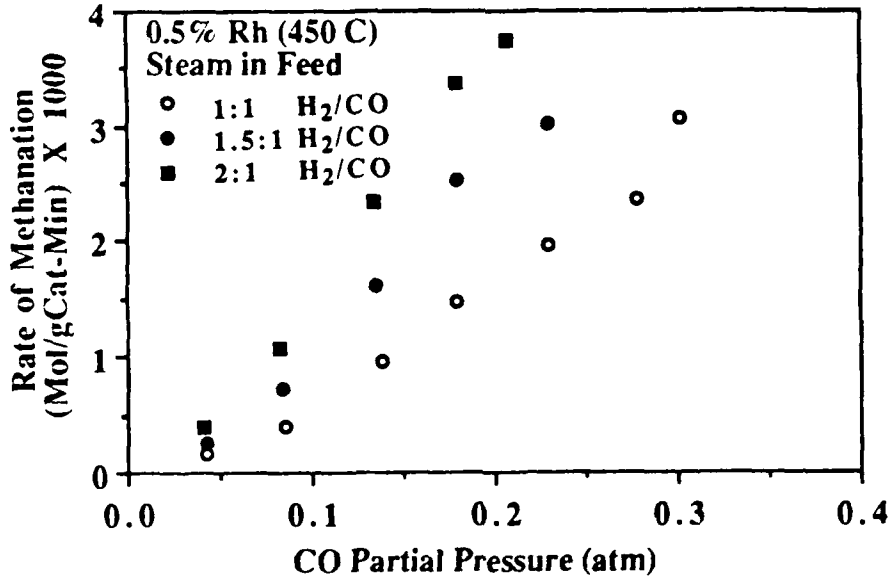


Figure 4.16
Methanation Rate versus CO Partial Pressure 450°C (Steam in Feed)

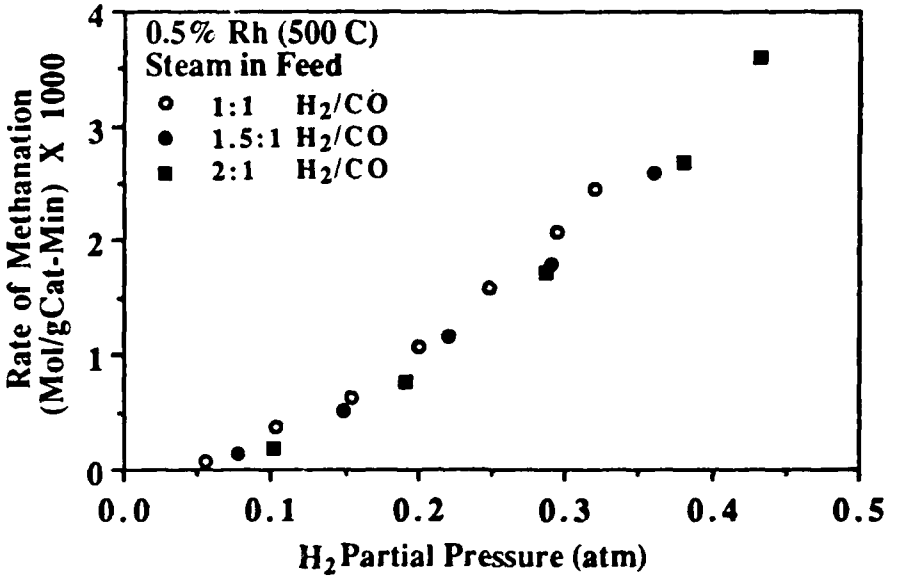


Figure 4.17
Methanation Rate versus H_2 Partial Pressure 500°C (Steam in Feed)

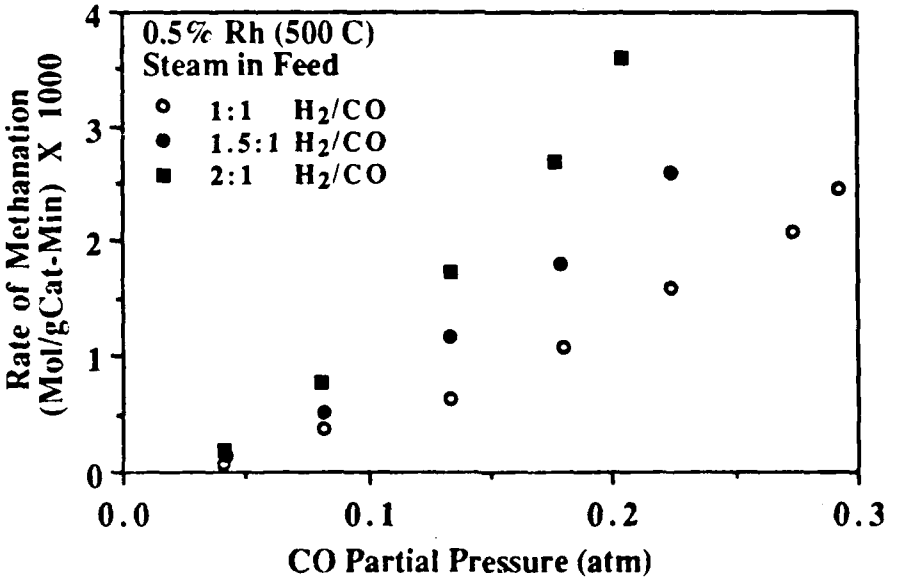


Figure 4.18
Methanation Rate versus CO Partial Pressure 500°C (Steam in Feed)

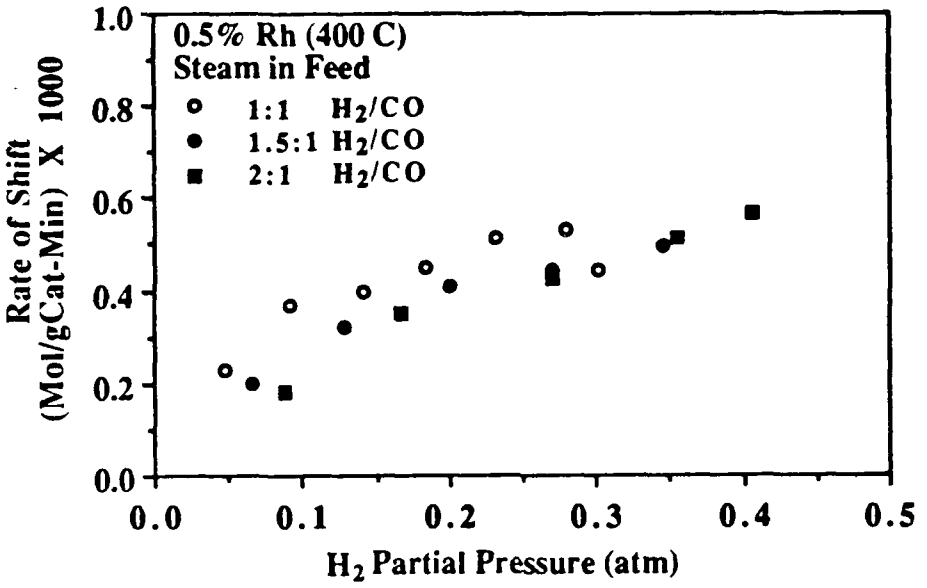


Figure 4.19
Shift Rate versus H_2 Partial Pressure 400°C (Steam in Feed)

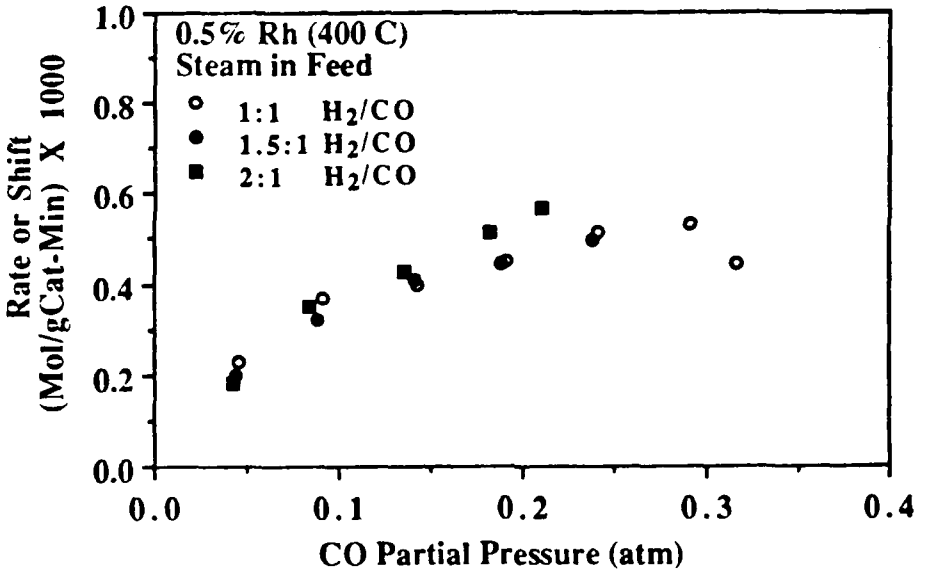


Figure 4.20
Shift Rate versus CO Partial Pressure 400°C (Steam in Feed)

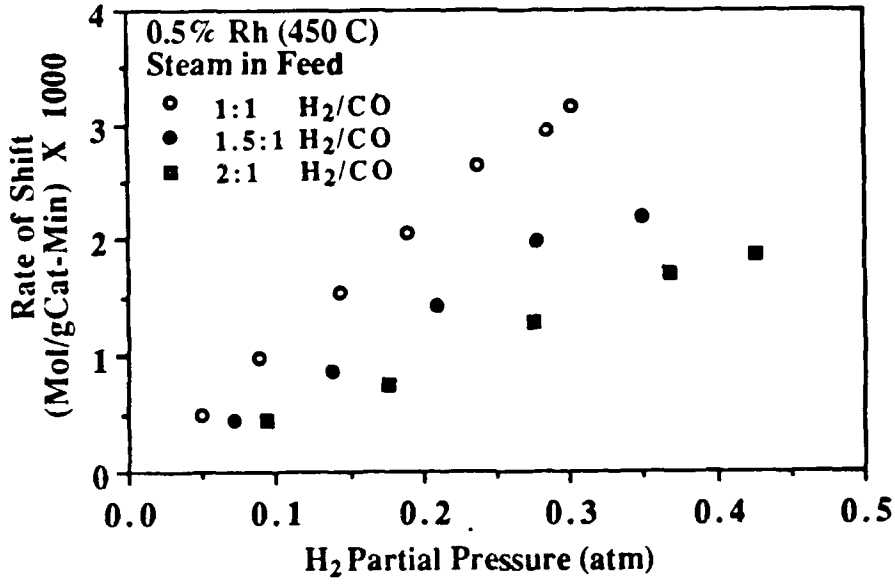


Figure 4.21
Shift Rate versus H_2 Partial Pressure 450°C (Steam in Feed)

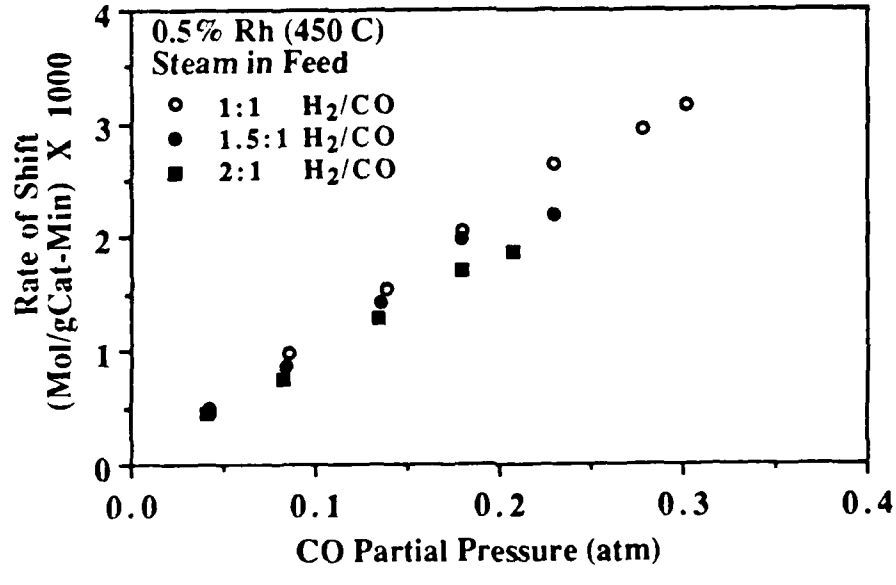


Figure 4.22
Shift Rate versus CO Partial Pressure 450°C (Steam in Feed)

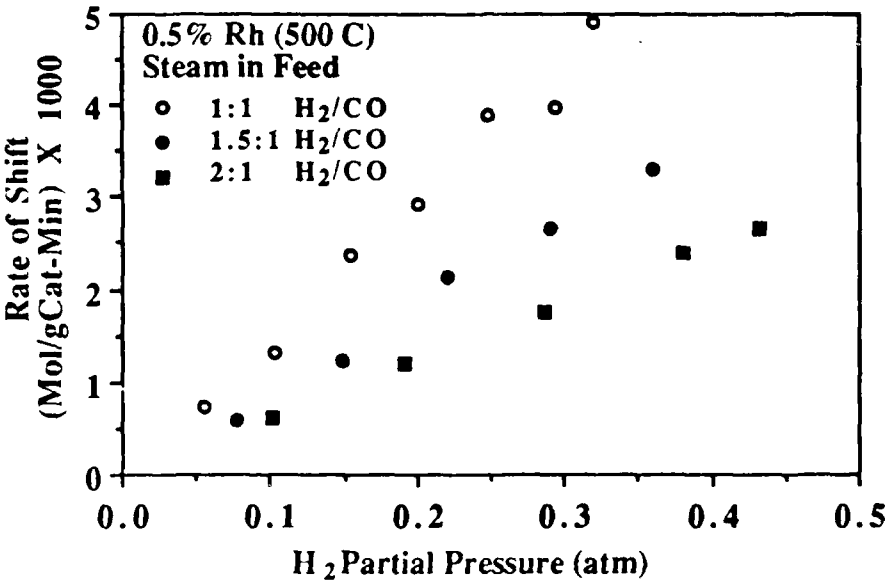


Figure 4.23
Shift Rate versus H_2 Partial Pressure 500°C (Steam in Feed)

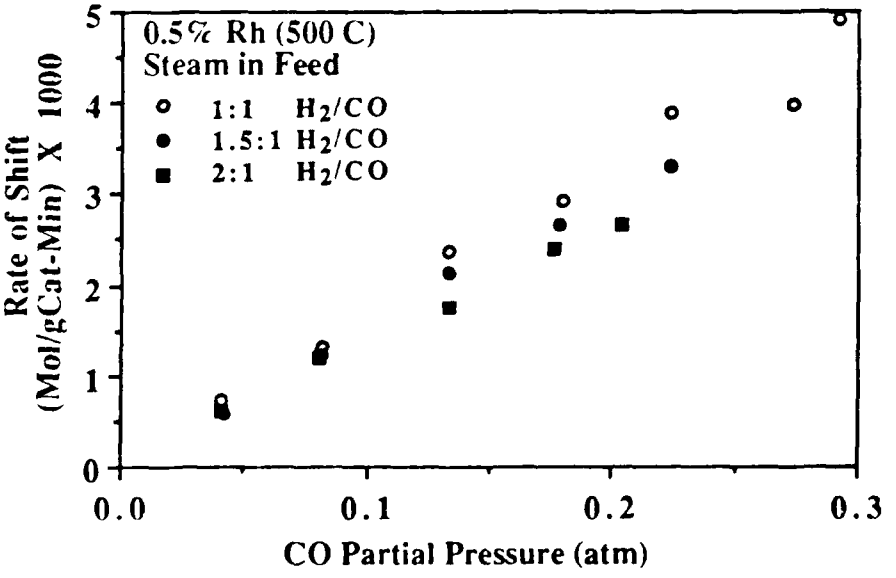


Figure 4.24
Shift Rate versus CO Partial Pressure 500°C (Steam in Feed)

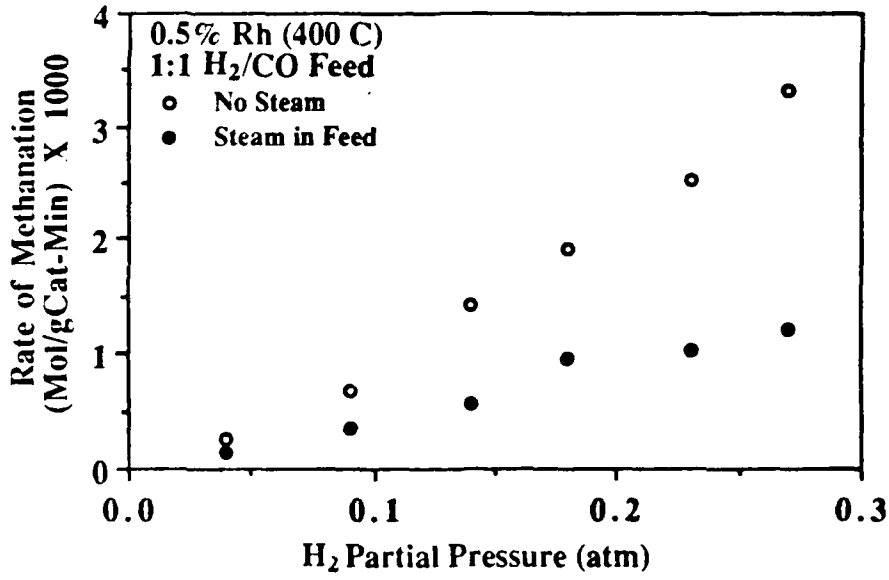


Figure 4.25
Comparison of Methanation Rate versus H_2 Partial Pressure
With and Without Steam 400°C

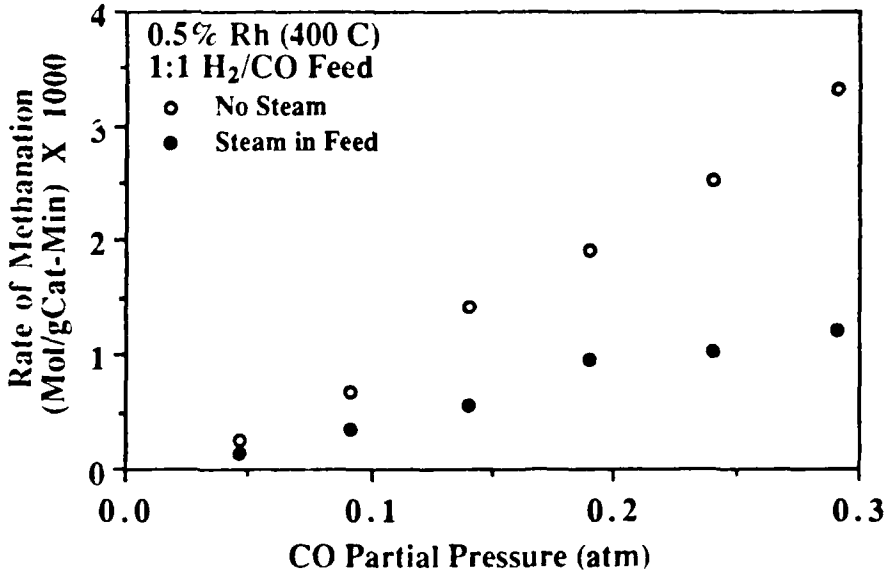


Figure 4.26
Comparison of Methanation Rate versus CO Partial Pressure
With and Without Steam 400°C

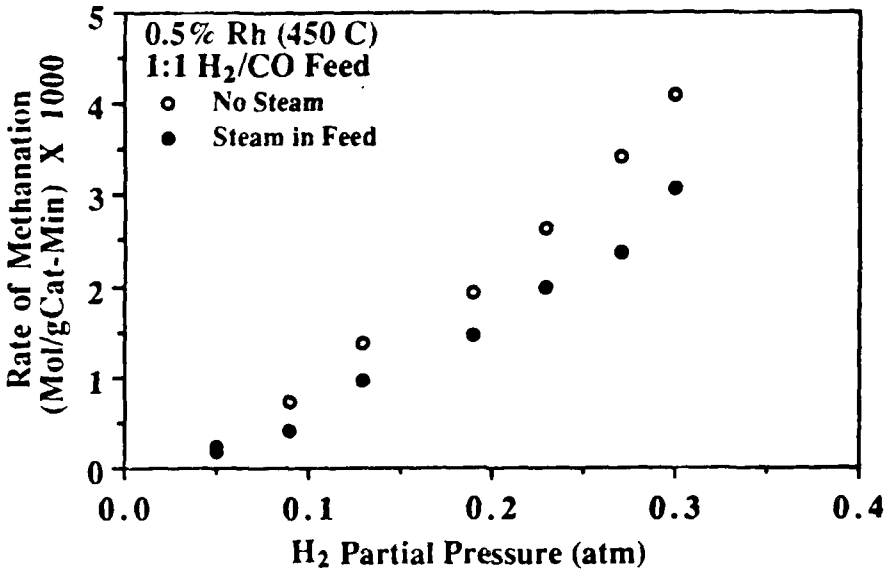


Figure 4.27
Comparison of Methanation Rate versus H_2 Partial Pressure
With and Without Steam 450°C

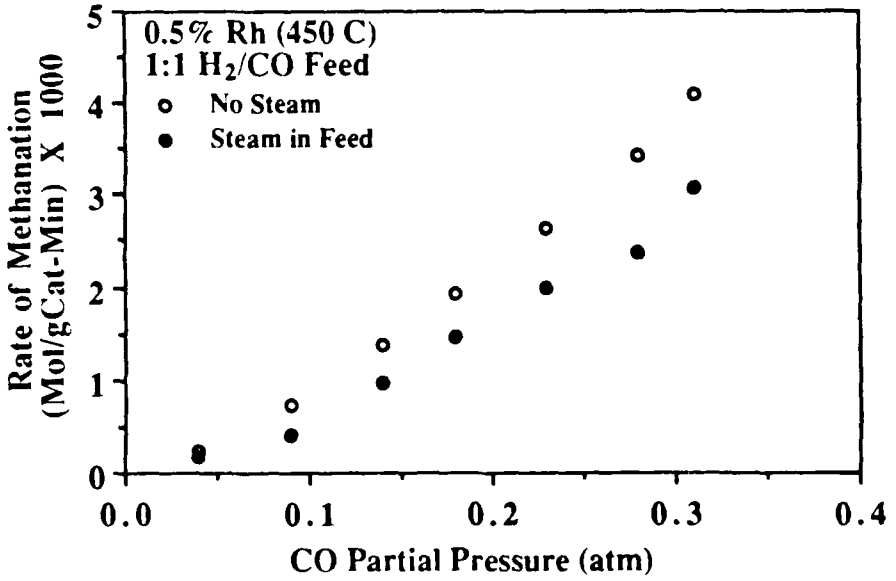


Figure 4.28
Comparison of Methanation Rate versus CO Partial Pressure
With and Without Steam 450°C

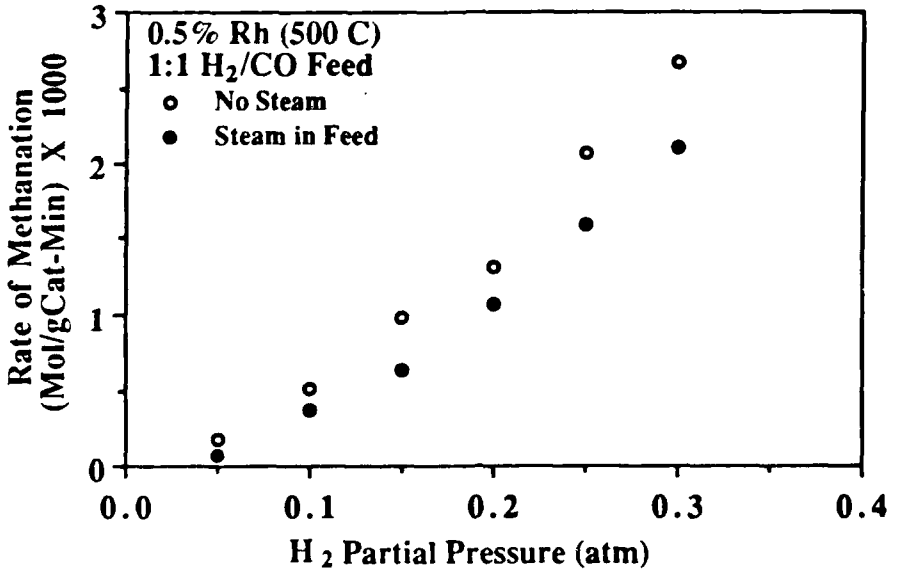


Figure 4.29
Comparison of Methanation Rate versus H_2 Partial Pressure
With and Without Steam 500°C

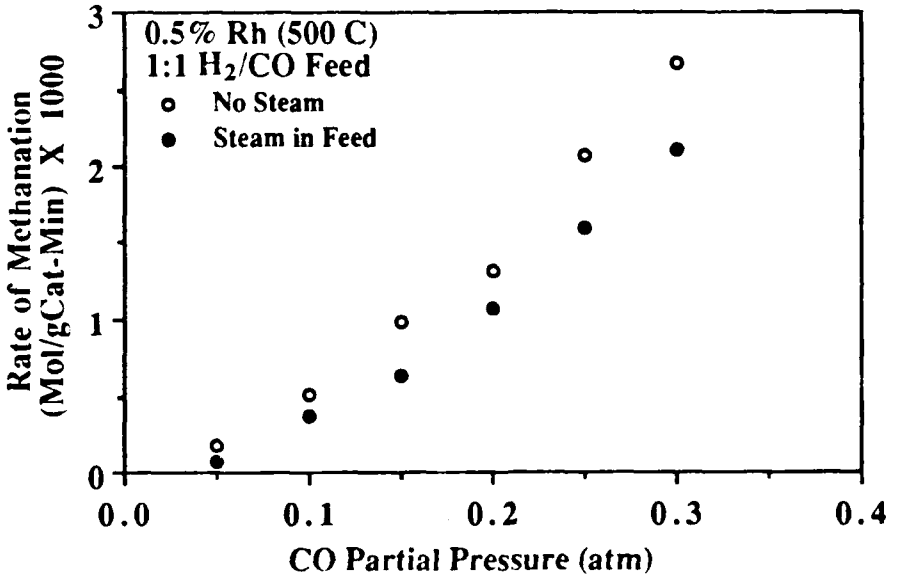


Figure 4.30
Comparison of Methanation Rate versus CO Partial Pressure
With and Without Steam 500°C

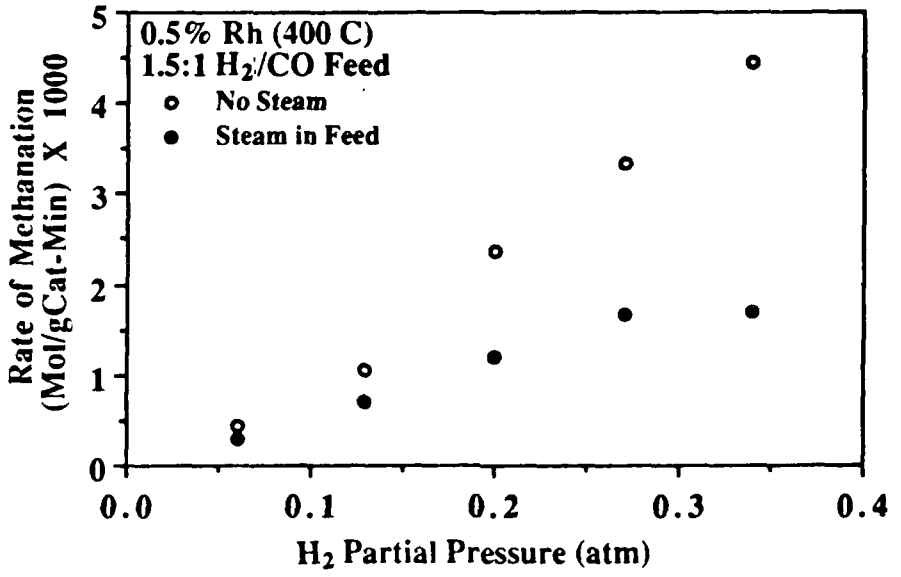


Figure 4.31
Comparison of Methanation Rate versus H_2 Partial Pressure
With and Without Steam 400°C

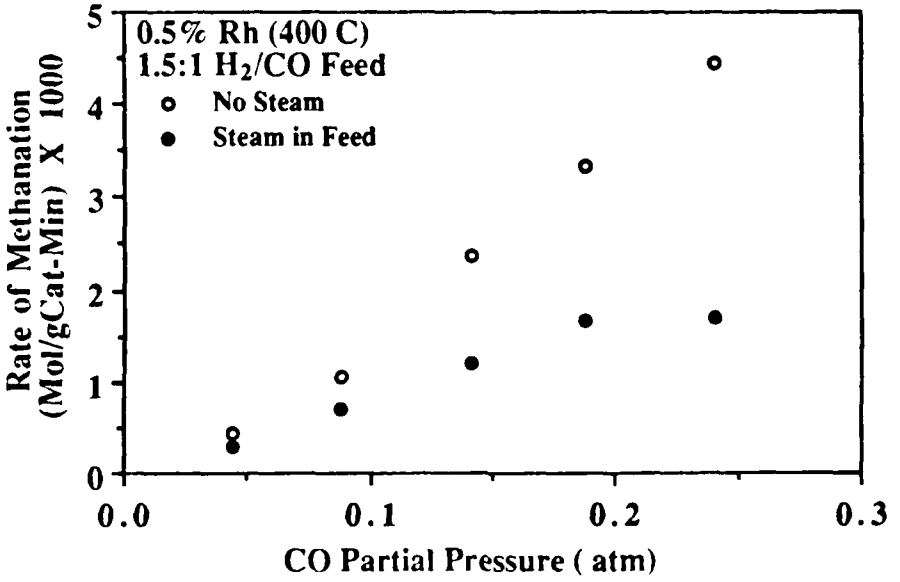


Figure 4.32
Comparison of Methanation Rate versus CO Partial Pressure
With and Without Steam 400°C

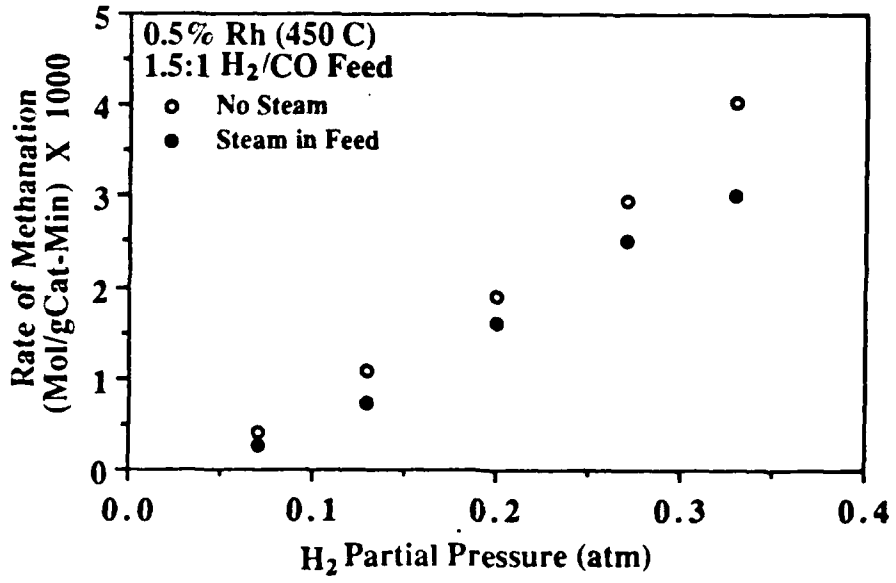


Figure 4.33
Comparison of Methanation Rate versus H_2 Partial Pressure
With and Without Steam 450°C

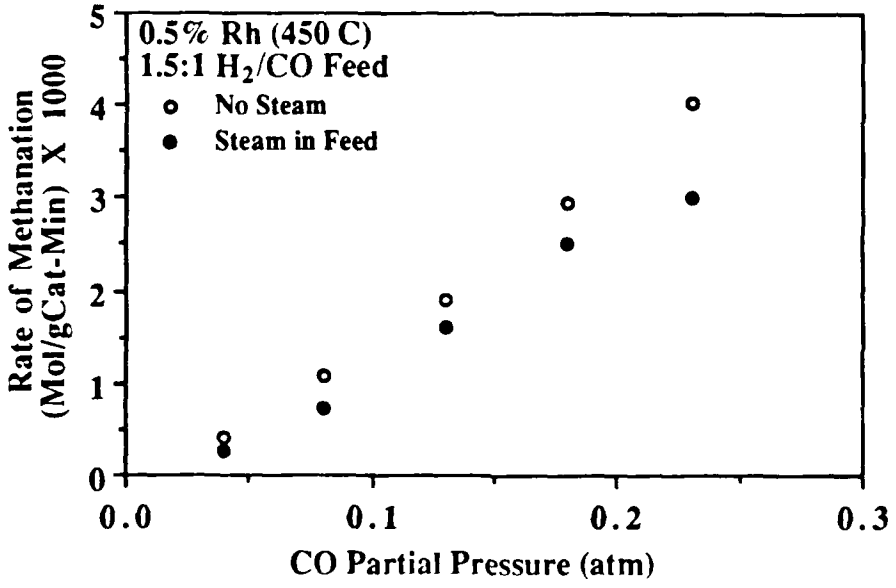


Figure 4.34
Comparison of Methanation Rate versus CO Partial Pressure
With and Without Steam 450°C

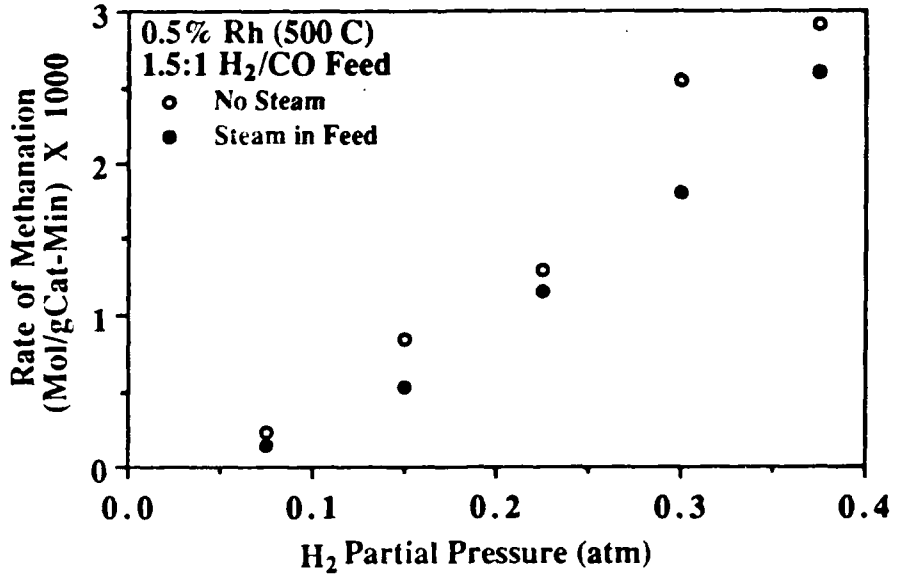


Figure 4.35
Comparison of Methanation Rate versus H_2 Partial Pressure
With and Without Steam 500°C

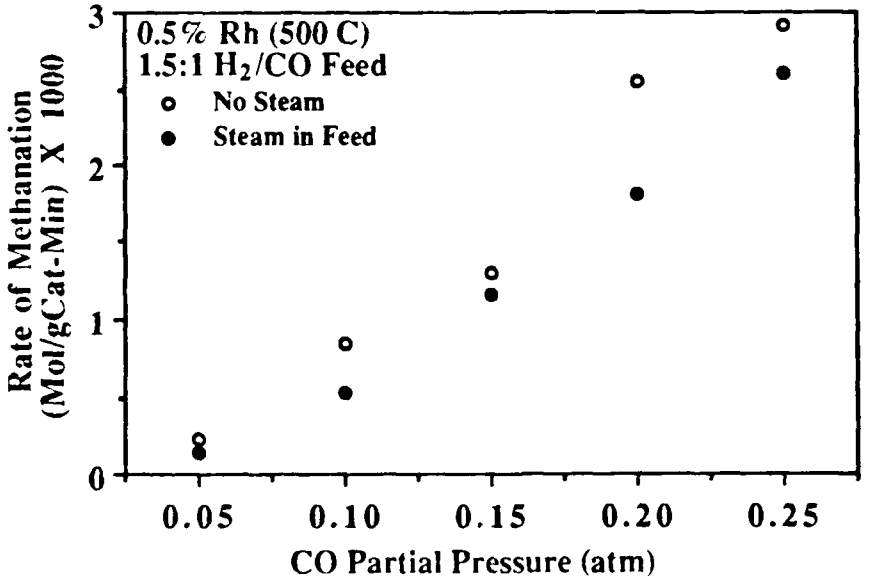


Figure 4.36
Comparison of Methanation Rate versus CO Partial Pressure
With and Without Steam 500°C

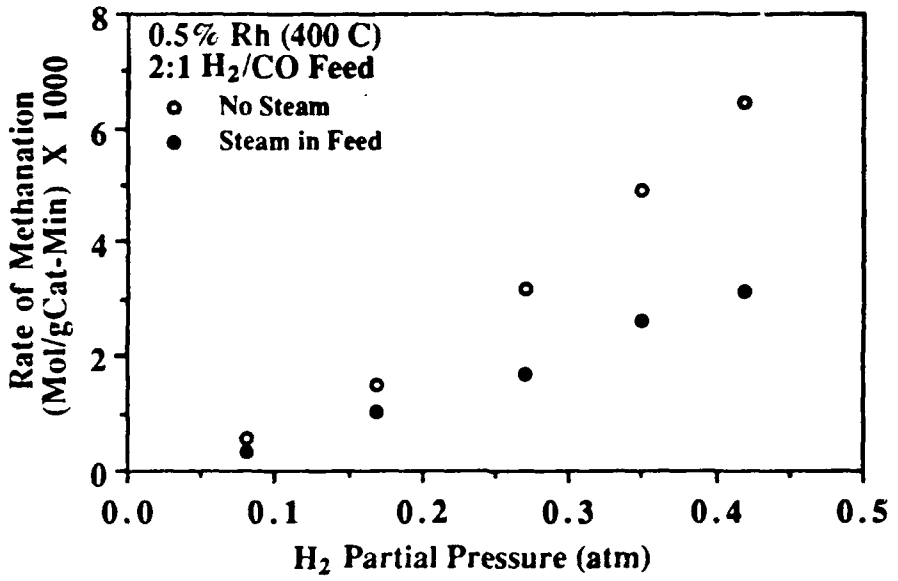


Figure 4.37
Comparison of Methanation Rate versus H_2 Partial Pressure
With and Without Steam 400°C

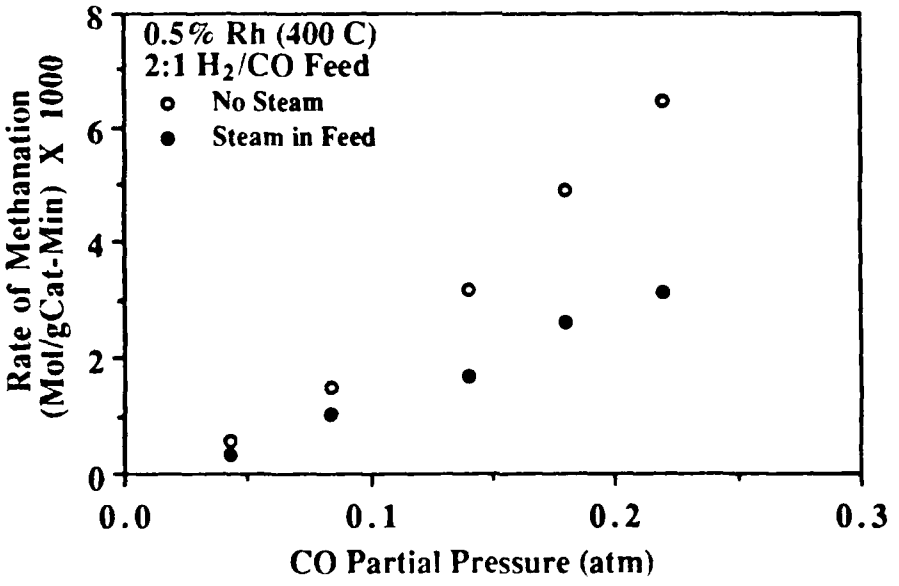


Figure 4.38
Comparison of Methanation Rate versus CO Partial Pressure
With and Without Steam 400°C

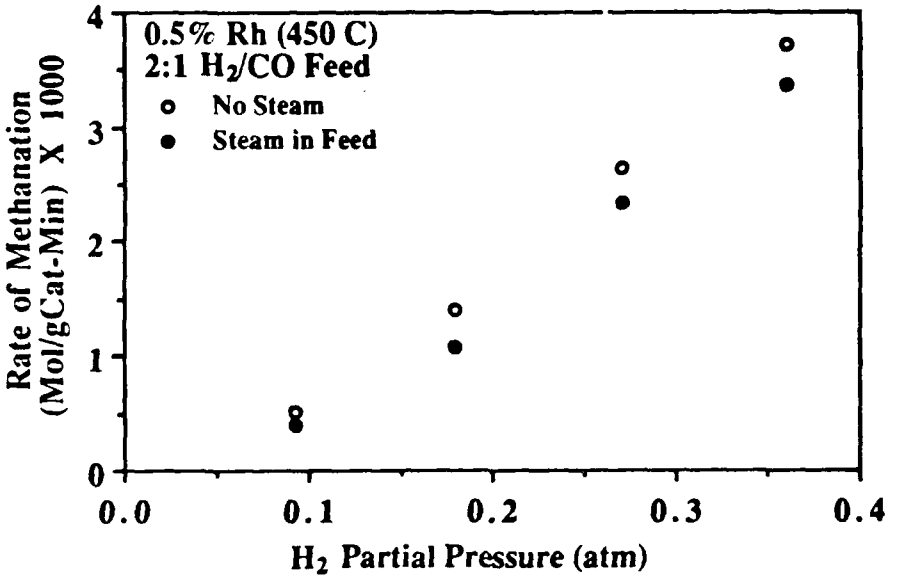


Figure 4.39
Comparison of Methanation Rate versus H_2 Partial Pressure
With and Without Steam 450°C

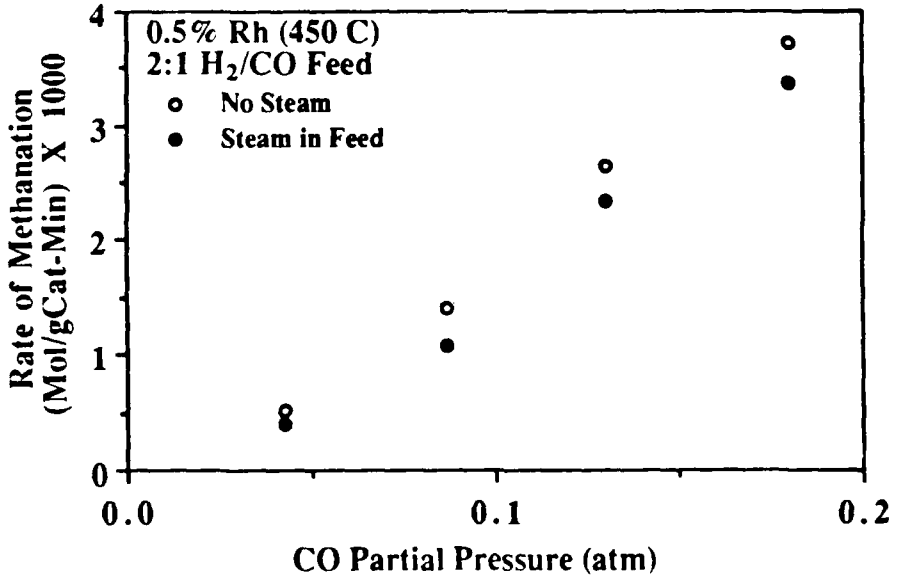


Figure 4.40
Comparison of Methanation Rate versus CO Partial Pressure
With and Without Steam 450°C

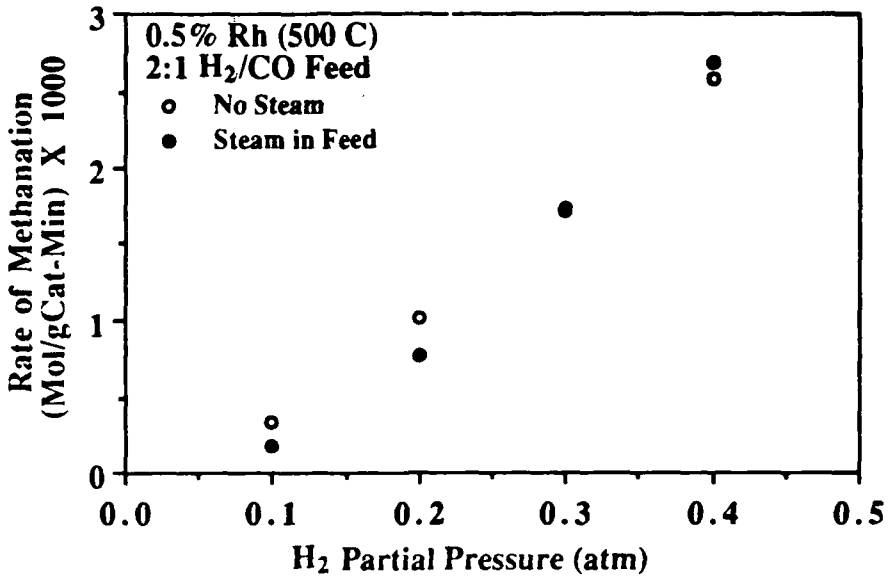


Figure 4.41
Comparison of Methanation Rate versus H_2 Partial Pressure
With and Without Steam 500°C

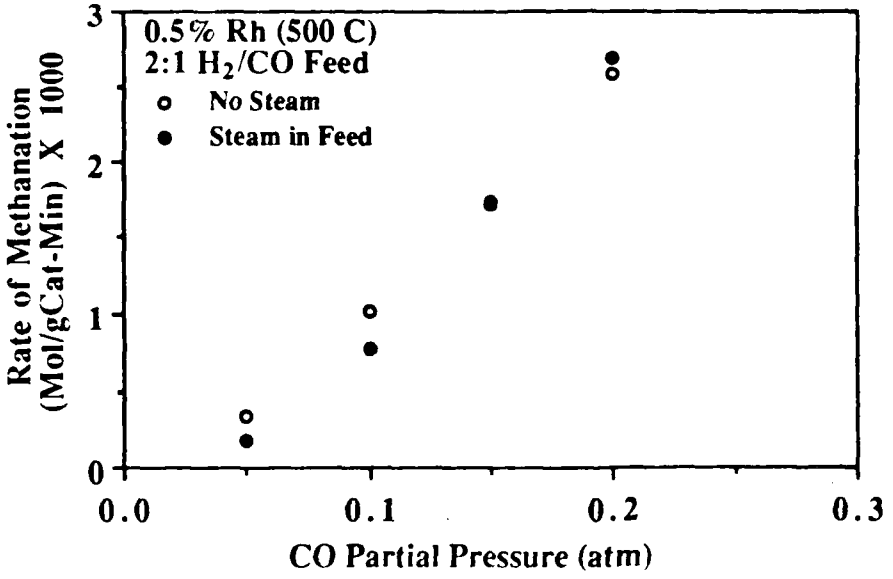


Figure 4.42
Comparison of Methanation Rate versus CO Partial Pressure
With and Without Steam 500°C

which is slowed by product inhibition. It can also be seen that the H_2/CO ratio did not affect the relative amount by which the rate of methanation dropped when steam was added to the feed. As the temperature increased, the relative drop in the rate of methanation, with the addition of steam to the feed, decreased. This effect could be caused by an increase in the rate of the water-shift reaction,

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad \{1.12\}$$

with the increased water concentration. This in turn increases the H_2/CO ratio through the consumption of CO and the production of H_2. The increase in the H_2/CO ratio favors the formation of methane {1.10} thus decreasing the relative rate difference. This hypothesis is supported by the fact that the amount of CO_2 in the product increased greatly with the addition of steam. It should also be noted that the amount of CO_2 produced per mole of CH_4 increased greatly when steam was added to the feed. This ratio increased with temperature, but increased more rapidly in the runs where steam was present in the feed to the reactor. The above facts show the importance of the water-shift reaction {1.12} at high temperatures and high water partial pressures.

Figures 4.43 to 4.60 show the effect of steam on the rate of the water-shift Reaction {1.12}. As with the rate of methanation, the relative difference between the rates of shift with and without steam is not affected by the H_2/CO ratio, but by temperature. Increase in the rate of shift with the addition of steam to the feed is evident at temperatures above 400°C. At a constant temperature and partial pressure of CO the rate of shift decreases with an increase in the H_2/CO ratio. As noted earlier, Reaction {1.10} is favored by an increase in the H_2/CO ratio. Increased consumption of CO by Reaction {1.10} at high H_2/CO ratios reduces the amount available for Reaction {1.12}, thus causing a decrease in the rate of Reaction {1.12}.

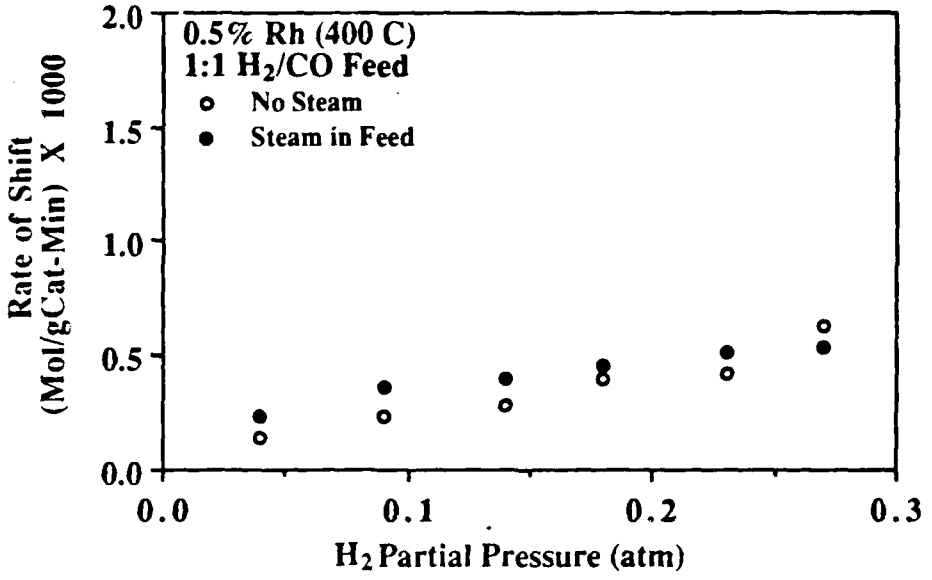


Figure 4.43
Comparison of Shift Rate versus H_2 Partial Pressure
With and Without Steam 400°C

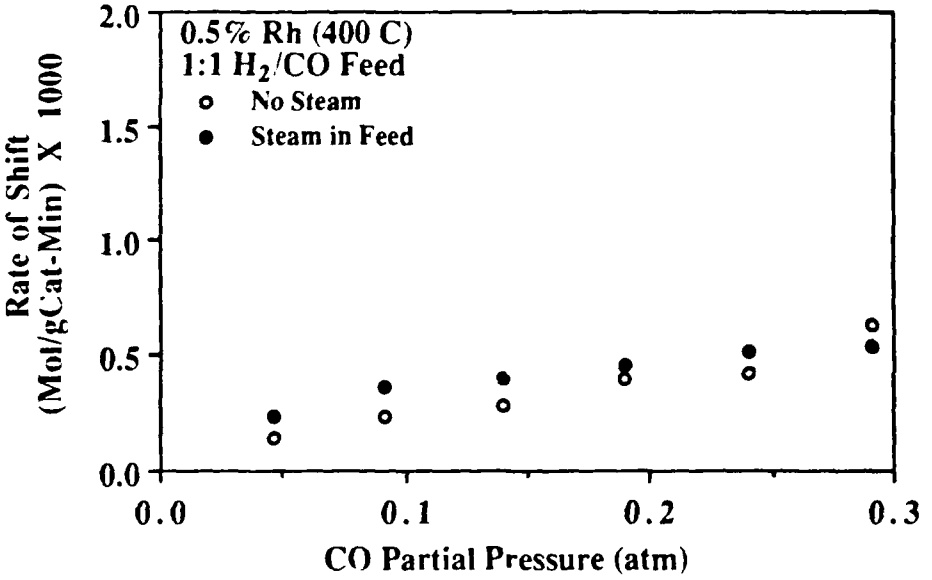


Figure 4.44
Comparison of Shift Rate versus CO Partial Pressure
With and Without Steam 400°C

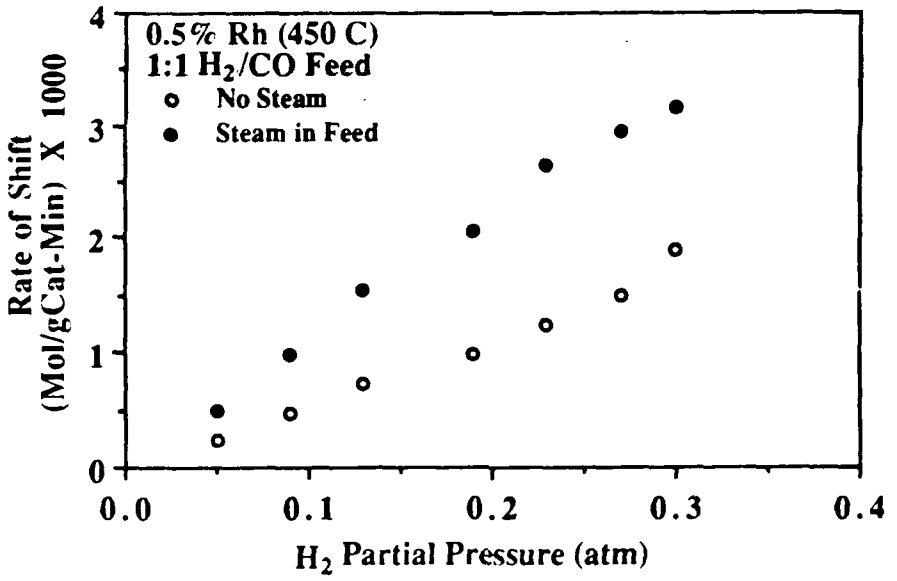


Figure 4.45
Comparison of Shift Rate versus H_2 Partial Pressure
With and Without Steam 450°C

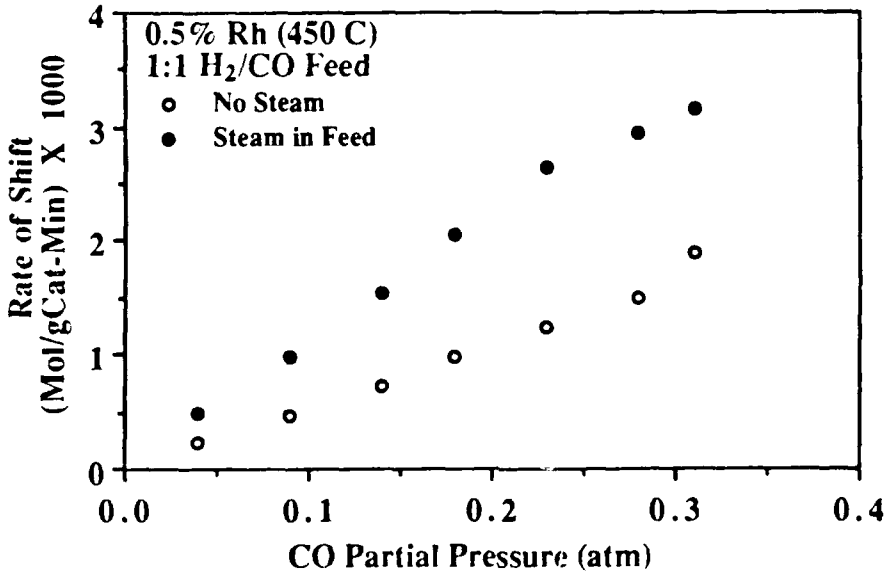


Figure 4.46
Comparison of Shift Rate versus CO Partial Pressure
With and Without Steam 450°C

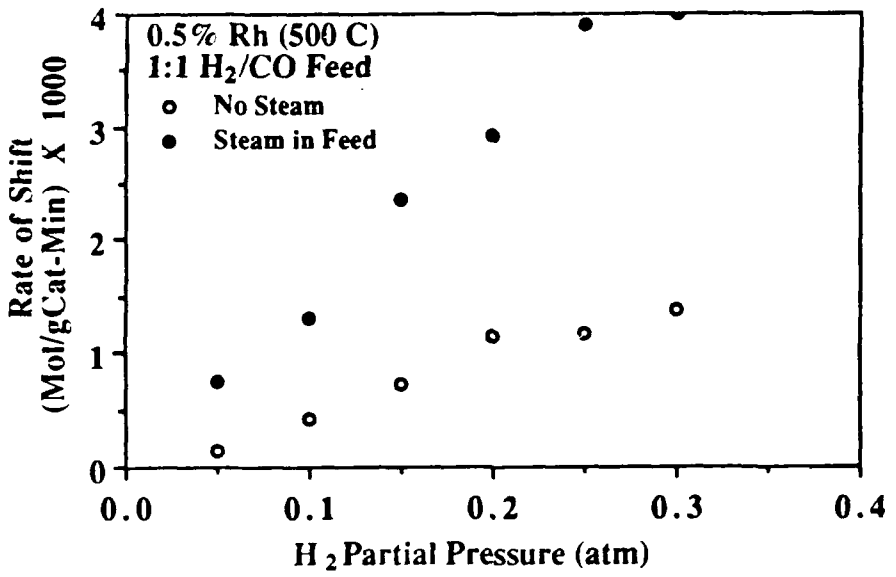


Figure 4.47
Comparison of Shift Rate versus H_2 Partial Pressure
With and Without Steam 500°C

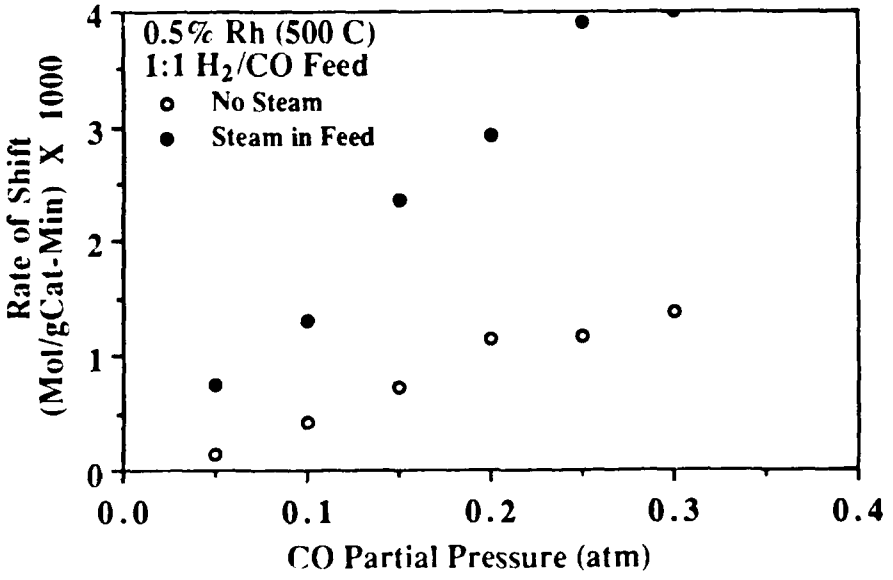


Figure 4.48
Comparison of Shift Rate versus CO Partial Pressure
With and Without Steam 500°C

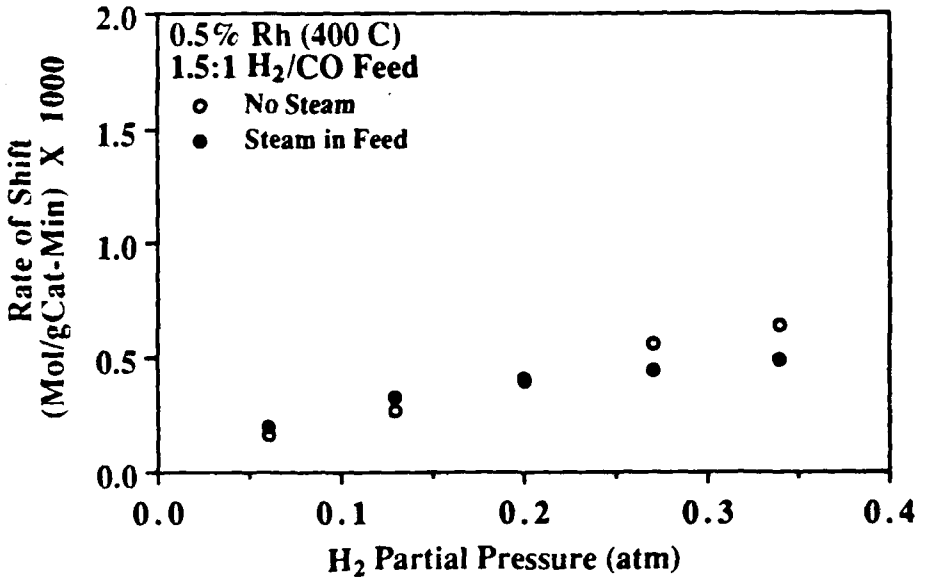


Figure 4.49
Comparison of Shift Rate versus H_2 Partial Pressure
With and Without Steam 400°C

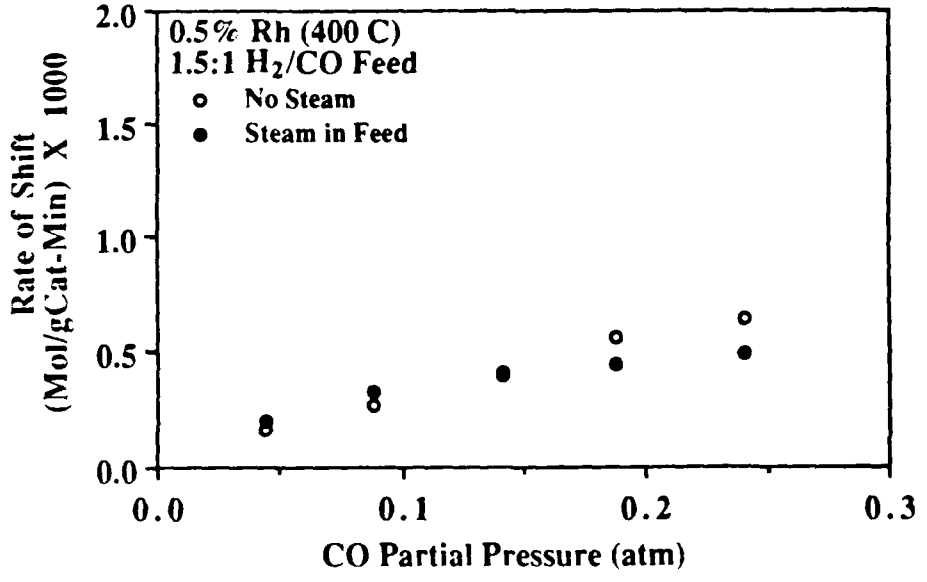


Figure 4.50
Comparison of Shift Rate versus CO Partial Pressure
With and Without Steam 400°C

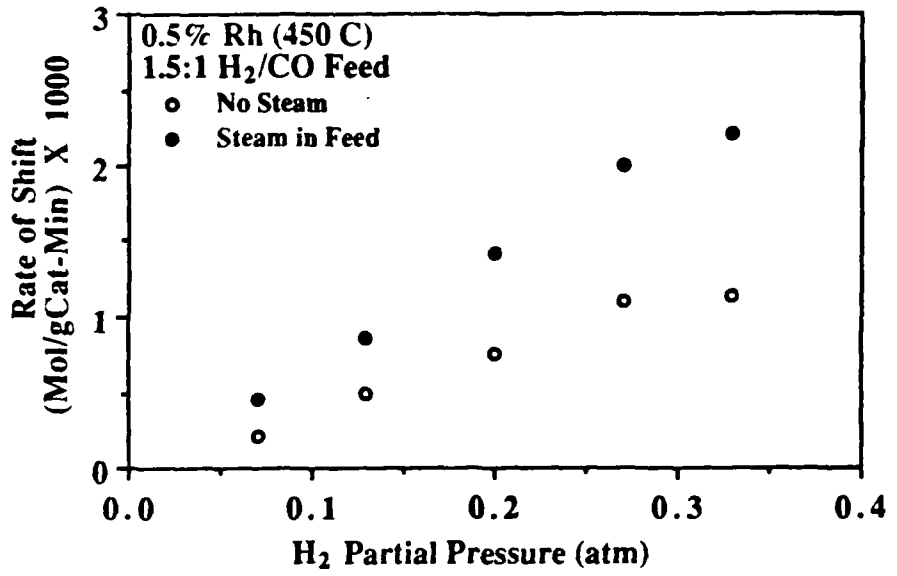


Figure 4.51
Comparison of Shift Rate versus H_2 Partial Pressure
With and Without Steam 450°C

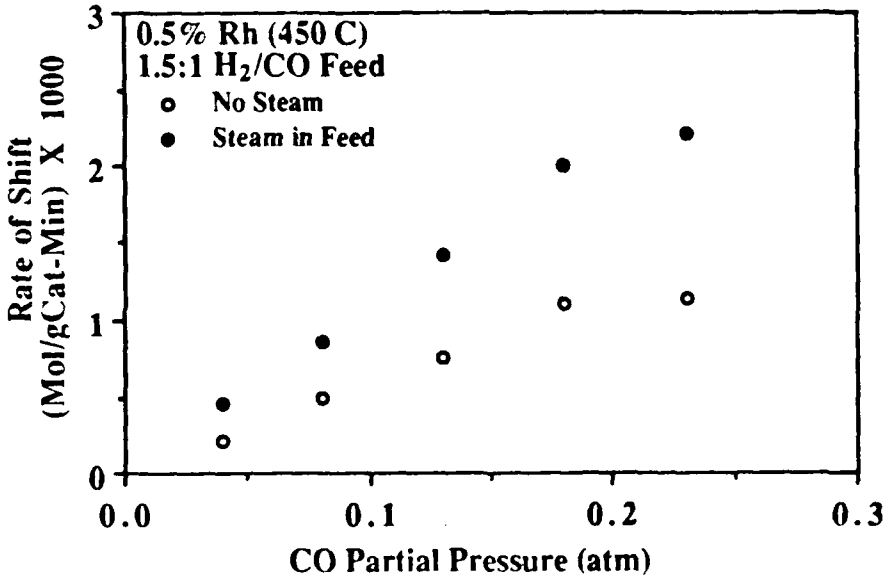


Figure 4.52
Comparison of Shift Rate versus CO Partial Pressure
With and Without Steam 450°C

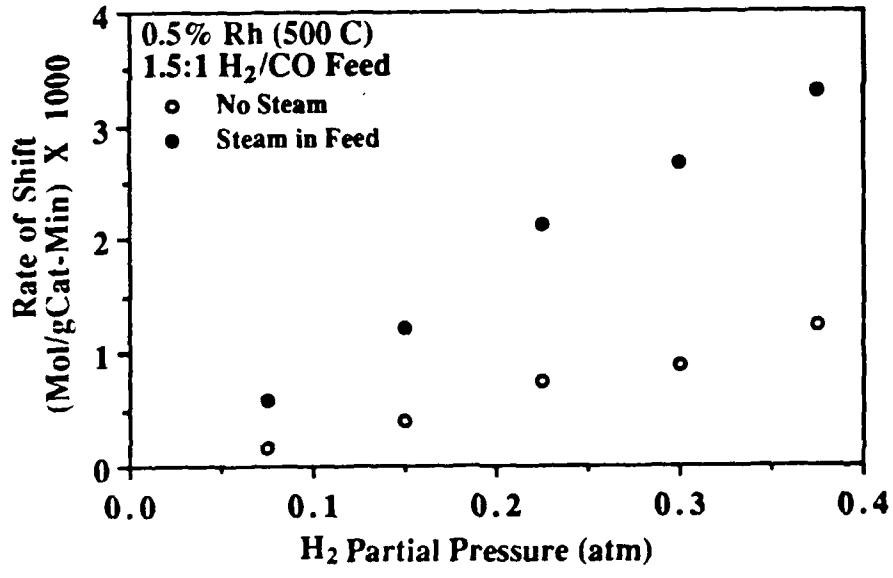


Figure 4.53
Comparison of Shift Rate versus H_2 Partial Pressure
With and Without Steam 500°C

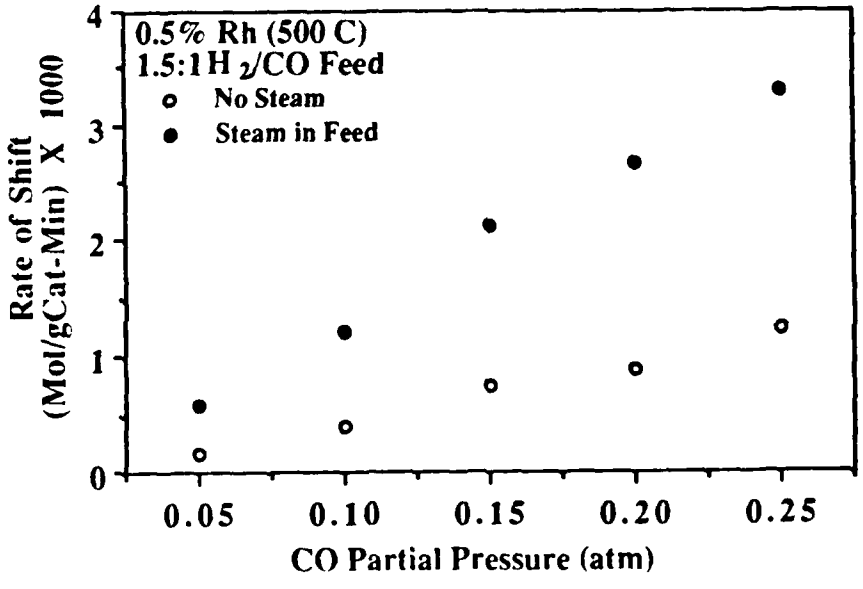


Figure 4.54
Comparison of Shift Rate versus CO Partial Pressure
With and Without Steam 500°C

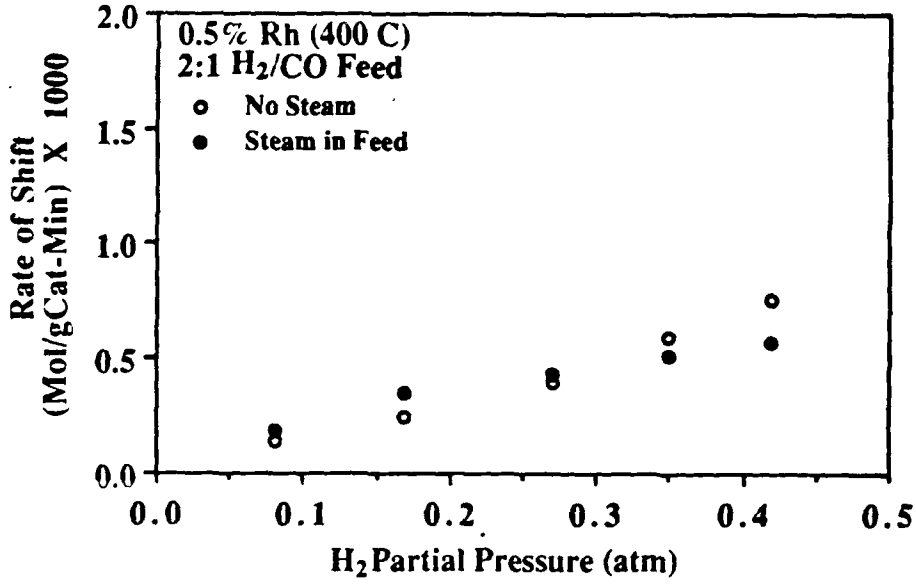


Figure 4.55
Comparison of Shift Rate versus H_2 Partial Pressure
With and Without Steam 400°C

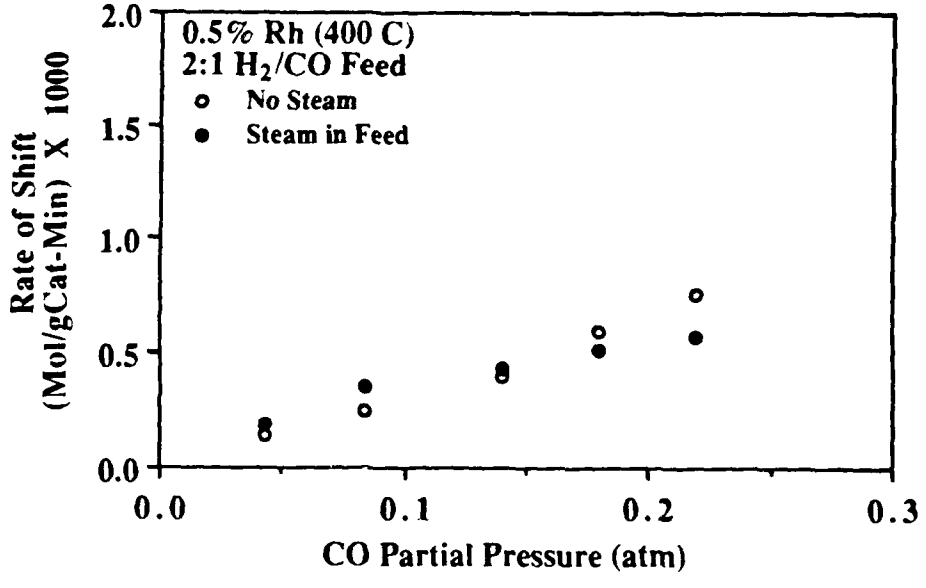


Figure 4.56
Comparison of Shift Rate versus CO Partial Pressure
With and Without Steam 400°C

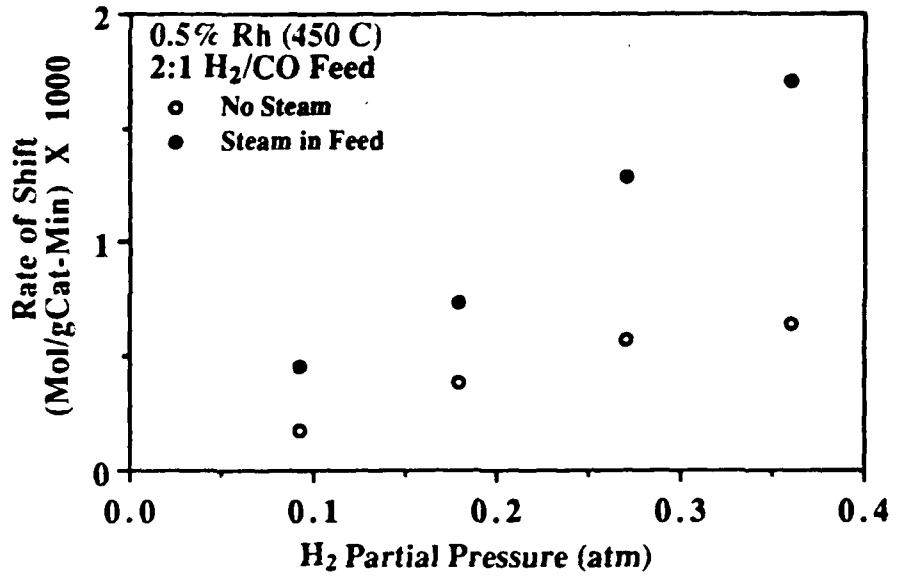


Figure 4.57
Comparison of Shift Rate versus H_2 Partial Pressure
With and Without Steam 450°C

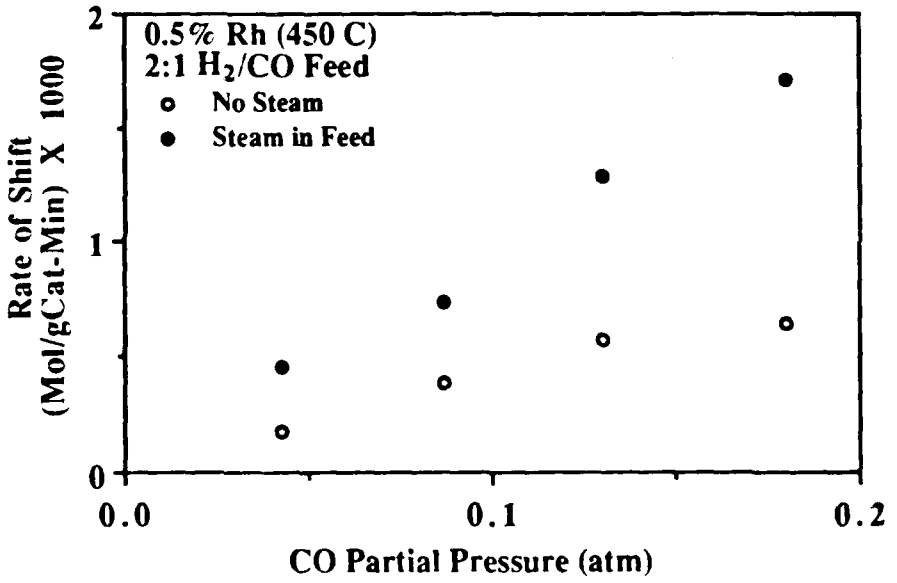


Figure 4.58
Comparison of Shift Rate versus CO Partial Pressure
With and Without Steam 450°C

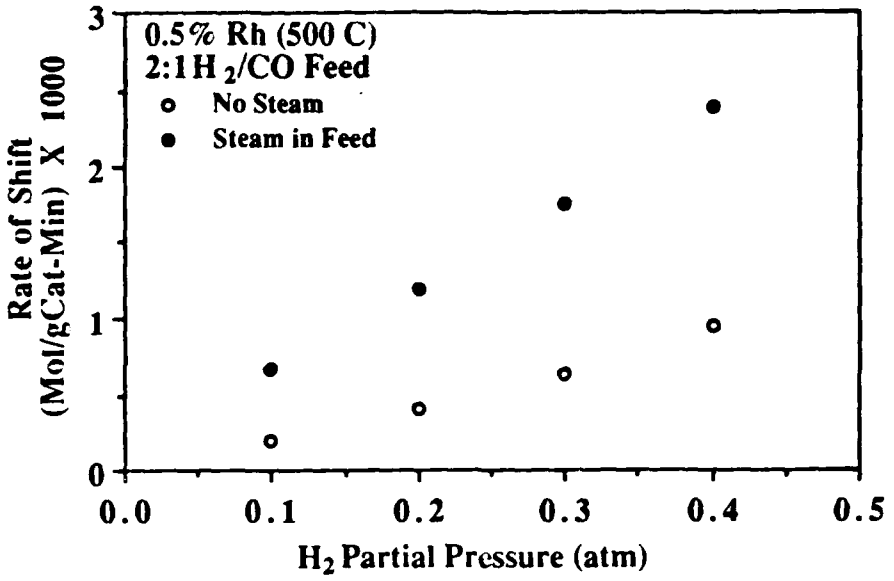


Figure 4.59
Comparison of Shift Rate versus H_2 Partial Pressure
With and Without Steam 500°C

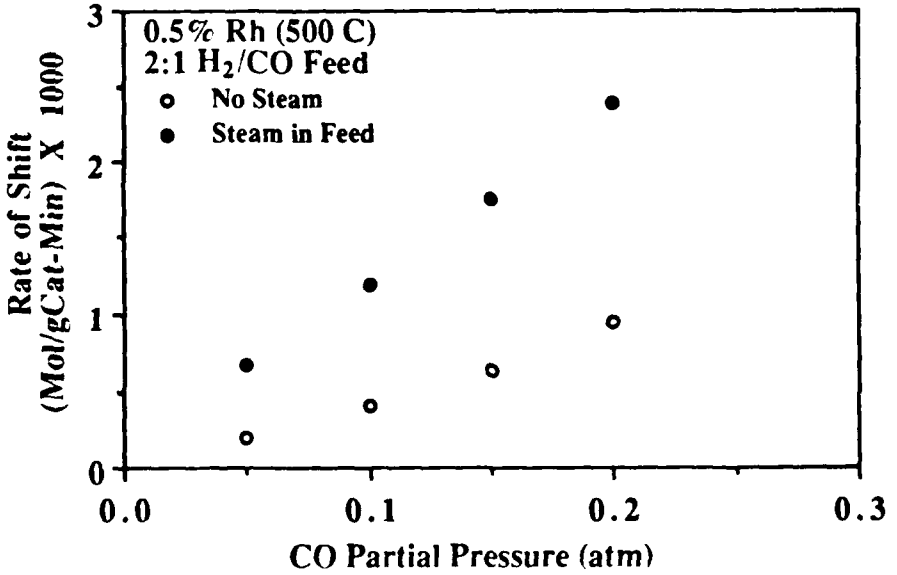


Figure 4.60
Comparison of Shift Rate versus CO Partial Pressure
With and Without Steam 500°C

4.5 Kinetic Expressions

A search of the literature shows that the application of rhodium to methanation has been studied, but this work was done at lower temperatures and at H_2/CO ratios higher than of interest here. An example is the work of Vannice [32,33], who studied the synthesis of hydrocarbons from hydrogen and carbon monoxide mixtures over Group VIII metals. One catalyst he looked at was 1% Rh on Al_2O_3. He conducted experiments over a range of H_2/CO ratios at 265°C. For the rate expression a power law was chosen of the form,

$$r_{CH_4} = Ae^{-Em/RT} P_{H_2}{}^X P_{CO}{}^Y \qquad (4.1)$$

where r_{CH_4} is the molecules of CH_4 formed per metal site per second. At 275°C Vannice observed a first-order dependence on the H_2 concentration and a zero order dependence on the CO concentration. For this work no steam was mixed with the feed. Vannice's work pointed out that rhodium did catalyze the methanation reaction, but his rate expression could not be used for comparison because of the dangers involved in extrapolating a power law expression out of the temperature and pressure range under which it was developed.

Initial forms of the kinetic expression were obtained using a linear regression program, which used the IMSL subroutine RLONE, to calculate the constants of a linearized Langmuir-Hinshelwood expression, which was thought to be of the right form. Different expressions were tried until one was found which fit the data from all of the runs over the temperature range studied. The final form of the kinetic expression was determined by Richardson [16].

For the 0.5% Rh catalyst, a Langmuir-Hinshelwood expression was obtained for the rate of methanation of the form,

$$\vec{R_M} = \frac{k_M K_{CO} P_{CO} P_H}{(1 + K_{CO} P_{CO})^2} \qquad \text{mole min}^{-1}\text{g(cat)}^{-1} \qquad (4.2)$$

Without steam in the feed, the rate constant k_M and the adsorption constant K_{CO} fit the Arrhenius expressions,

$$k_M = 7.94 \times 10^{-2}\, e^{-2519/RT} \qquad (4.3)$$

$$K_{CO} = 4.58 \times 10^{-2}\, e^{23795/RT} \qquad (4.4)$$

With steam added to the feed in a 1:1 ratio with CO, the constants fit the Arrhenius expressions,

$$k_M = 5.57 \times 10^{-2}\, e^{-31086/RT} \qquad (4.5)$$

$$K_{CO} = 1.92 \times 10^{-5}\, e^{71268/RT} \qquad (4.6)$$

For the water-shift reaction, {1.12} two separate rate equations were obtained for the cases of no steam in the feed and steam in a 1:1 ratio with CO. For the case of no steam in the feed a first-order dependence on H_2O was observed of the form,

$$\vec{R_S} = k_{S1} P_{H_2O} \qquad \text{mole min}^{-1}\text{g(cat)}^{-1} \qquad (4.7)$$

$$k_{S1} = 45.18\, e^{-38228/RT} \qquad (4.8)$$

For the case of steam in the feed, a first-order dependence on H_2O was also observed of the form,

$$\vec{R_S} = k_{S2} P_{H_2O} \qquad \text{mole min}^{-1}\text{g(cat)}^{-1} \qquad (4.9)$$

$$k_{S2} = 3.25 \times 10^{3}\, e^{-78368/RT} \qquad (4.10)$$

with all P's in atmospheres and R = 8.314 J mole^{-1}K^{-1}

These rate equations apply only in the temperature range 400 to 500°C. All of these rate expressions were found to fit the experimental data very well. The regression coefficients for Equations (4.2), (4.7), and (4.9) appear in Table 4.2. Comparisons of the calculated rates of methanation and shift can be seen in Tables 4.3 and 4.4 respectively.

Table 4.2

Regression Coefficients
(* Steam in Feed)

Equation	Regression Coefficient	
$\vec{R}_M = \frac{k_M K_{CO} P_{CO} P_{H_2}}{(1 + K_{CO} P_{CO})^2}$	0.9854	(4.2)
	0.9692 *	
$\vec{R}_S = k_{S1} P_{H_2O}$	0.8923	(4.7)
$\vec{R}_S = k_{S2} P_{H_2O}$	0.9716 *	(4.9)

Table 4.3

Comparison of Calculated Methanation Rate to Experimental Results
(* Steam in Feed)

Temperature (°C)	P_{H_2}	P_{CO}	k_M	K_{CO}	Rate x 10^3 Calculated	Rate x 10^3 Experimental
400	0.223	0.242	0.0506	3.218	2.779	2.534
400	0.179	0.193	0.0506	3.218	2.142	1.921
400*	0.346	0.238	0.0215	6.520	1.775	1.708
400*	0.089	0.043	0.0215	6.520	0.238	0.349
450	0.329	0.232	0.0522	2.398	3.947	4.035
450	0.267	0.136	0.0522	2.398	2.586	2.645
450*	0.190	0.184	0.0316	2.702	1.332	1.463
450*	0.050	0.043	0.0316	2.702	0.147	0.161
500	0.129	0.088	0.0537	1.856	0.835	0.849
500	0.047	0.046	0.0537	1.856	0.183	0.175
500*	0.220	0.134	0.0442	1.255	1.197	1.165
500*	0.103	0.082	0.0442	1.255	0.385	0.375

Table 4.4

Comparison of Calcu'ated Shift Rate to Experimental Results
(* Steam in Feed)

Temperature (°C)	P_{H_2O}	k_S	Rate x 10^3 Calculated	Rate x 10^3 Experimental
400	0.022	0.04880	1.074	0.919
400	0.005	0.04880	0.244	0.231
400*	0.207	0.00269	0.557	0.453
400*	0.101	0.00269	0.272	0.367
450	0.010	0.07826	0.783	0.761
450	0.002	0.07826	0.187	0.174
450*	0.250	0.00709	1.773	1.881
450*	0.050	0.00709	0.355	0.452
500	0.001	0.11807	0.118	0.172
500	0.016	0.11807	1.889	1.864
500*	0.242	0.01647	3.986	3.899
500*	0.045	0.01647	0.741	0.611

Since it was not possible to derive a suitable rate expression with one set of constants, two separate sets of rate and equilibrium constants for the methanation and shift rate equations are necessary. The expressions must thoroughly describe the methanation and shift kinetics for the cases of no steam in the feed and steam in a 1:1 ratio with CO. Several forms of the Langmuir-Hinshelwood expression were tried, but none correlated with the experimental data. A similar situation arose in the study of CO_2 reforming on the 0.5% Rh catalyst by Paripatyadar [1]. Here again two separate sets of constants were needed to describe the kinetics when steam was absent or present in the reactor feed.

4.6 Kinetic Expressions at High Conversions

Most of the experimental runs were done at low conversions so the kinetics of the methanation reaction {1.10} could be studied. Equations (4.2) to (4.10) all reflect kinetics

at low conversions and must be modified to describe kinetics at high conversion. To accomplish this additional data was taken at high conversions with steam in the feed at a 1:1 ratio with CO (Appendix C).

Near equilibrium, the rate of methanation is slowed. To account for this, reverse terms were needed in the kinetic expressions, resulting in the equations[16],

$$R_M = \vec{R_M} \left[1 - \frac{P_{CH_4} P_{H_2O}}{K_M P_{CO} P_{H_2}^3} \right] \tag{4.11}$$

$$R_S = \vec{R_S} \left[1 - \frac{P_{CO_2} P_{H_2}}{K_S P_{CO} P_{H_2O}} \right] \tag{4.12}$$

where K_M and K_S are the equilibrium constants of the methanation and shift reactions respectively. The above equations gave higher rates than measured at high conversions. At near complete conversion large amounts of CH_4 and CO_2 are present. The presence of high concentrations of these gases would inhibit the methanation and shift reactions respectively. This inhibition is not accounted for in Equations (4.11) and (4.12). To provide for this, inhibition terms were added to the denominators of the rate equations and the constants fitted to the high conversion data. For the case of steam in the feed the rate of methanation is expressed,

$$R_M = k_M K_{CO} P_{H_2} P_{CO} \frac{1 - \frac{P_{CH_4} P_{H_2O}}{K_M P_{CO} P_{H_2}^3}}{(1 + K_{CO} P_{CO} + K_{MCH_4} P_{CH_4} + K_{MCO_2} P_{CO_2})^2} \tag{4.13}$$

and the rate of shift,

$$R_S = k_S P_{H_2O} \frac{1 - \frac{P_{CO_2} P_{H_2}}{K_S P_{CO} P_{H_2O}}}{(1 + K_{SCH_4} P_{CH_4} + K_{SCO_2} P_{CO_2})} \tag{4.14}$$

with all of the constants the same as Equations (4.3), (4.4), and (4.8) along with

$$K_{MCH_4} = 0.552\ e^{13743/RT} \tag{4.14}$$

$$K_{MCO_2} = 0.559\ e^{10700/RT} \tag{4.15}$$

$$K_{SCH_4} = 0.974\ e^{13743/RT} \tag{4.16}$$

$$K_{SCO_2} = 0.978\ e^{10700/RT}. \tag{4.17}$$

Data was not available to fit the constants for the case without steam, but it is reasonable to use the additional constants from the steam case to get,

$$R_M = k_M K_{CO} P_{H_2} P_{CO} \frac{1 - \dfrac{P_{CH_4} P_{H_2O}}{K_M P_{CO} P_{H_2}^3}}{(1 + K_{CO} P_{CO} + K_{MCH_4} P_{CH_4} + K_{MCO_2} P_{CO_2})^2} \tag{4.18}$$

$$R_S = k_S P_{H_2O} \frac{1 - \dfrac{P_{CO_2} P_{H_2}}{K_S P_{CO} P_{H_2O}}}{(1 + K_{SCH_4} P_{CH_4} + K_{SCO_2} P_{CO_2})} \tag{4.19}$$

which were later compared with data from the integral reactor of the Screening Unit [14] and found to be in good correlation [16].

4.7 Lifetime Study

One lifetime study was performed on the 0.5% Rh catalyst. The problem with the iron contamination in the support was known, but it was still desired to test the catalyst performance. For this study the reactor was loaded with 1.5238g of catalyst and run for 100 hours at 400°C and 400 sccm of feed, composed of 30% CO, 30% H_2O, 30% H_2,

and 10% N_2. Representative data appears in Appendix F. At completion of the 100 hours, the catalyst was checked for physical damage. As seen in Figure 4.61, the catalyst showed a slight deactivation. This was thought to have been caused by the iron impurity in the alumina support. Physical examination of the catalyst revealed a very light deposit of carbon on the catalyst surface. Without the impurity in the alumina support, it is felt that the catalyst would have a very long lifetime and remain free of carbon.

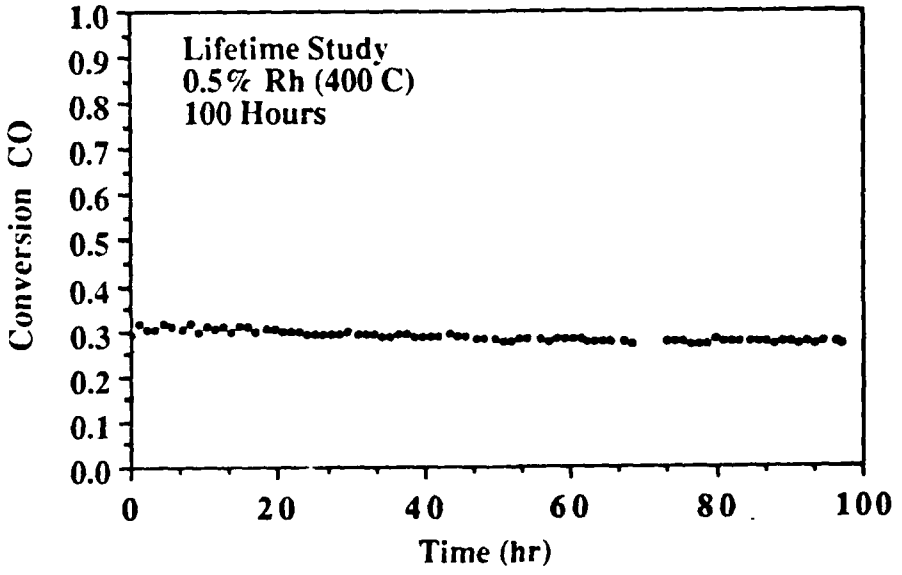


Figure 4.61
Lifetime Study 400°C

CHAPTER 5

RESULTS AND DISCUSSION - 70% Ni

This chapter focuses on the experimental results for the 70% Ni catalyst. The experimental procedure is reviewed and any deviations or difficulties included. Experimental results, kinetic expressions, and results of the lifetime study are presented and discussed.

5.1 Review of Experimental Procedure

The experimental procedure for the testing of the 70% Ni catalyst remained the same as described in Chapter 3, except experiments were not conducted at 450°C due to carbon formation on the catalyst at high temperatures.

An eight hour reduction period was believed to be too long, so periods of four and six hours, at 400°C and H_2 flow of 50 sccm, were tried. In both cases the reduction period proved too short as evidenced by low initial catalyst activity. Periods longer than eight hours were tried, but failed to increase initial catalytic activity. The eight hour reduction period proved necessary for proper catalyst reduction.

Maintenance practices for the system are well established, and are described in Chapter 4. During this study no additional modifications were made to the equipment.

5.2 Data Analysis

Processing of the experimental data remained the same. All of the data for experimental runs on the 70% Ni catalyst are tabulated in Appendix D.

5.2.1 Definitions

Data presented in Appendix D use the same definitions of conversion, yield and correction factor. These definitions are clearly stated in Section 4.2.1.

5.2.2 Sources of Deactivation

The formation and elimination of iron carbonyl from the reactor feed was discussed in Section 2.2. This cause of deactivation was detected at the start of the experimental work on the 0.5% Rh catalyst and eliminated.

Formation of carbon on the 70% Ni catalyst made study of kinetics difficult. As mentioned in section 3.4, it was hoped that the addition of steam to the feed stream would reduce the amount of carbon formed. Bartholomew [6] found that higher partial pressures of steam in methanator feed gases reduced, and even eliminated the formation of carbon. Addition of steam to the feed eliminated carbon fouling at 300 and 350°C, but the effect greatly decreased at higher temperatures. Little deactivation was noticed, and carbon formation limited to the darkening of the pellet surface at 300 and 350°C. At 400°C the pellets had a light carbon coat and lost their physical strength after only 42 hours of operation. This problem was more severe at high CO partial pressures (0.3 atm) and less severe at lower partial pressures (0.05 atm). At 500°C and 26 hours of operation, the pellets were very brittle and had a fuzzy layer of filamentous carbon on the surface. At both 400°C and 500°C the catalyst did not decrease in activity, despite the carbon deposited on the surface, but increased in activity after 40 and 24 hours of operation respectively. The structure of the pellet was weakened by the formation of carbon. It was thought that the carbon formation exerted pressure on the support and broke the pellet, thus exposing more active metal, which in turn caused an increase in activity. More catalyst activity is always desired, but the destruction of the alumina support in the process cannot be tolerated.

Weakening of the catalyst support has been attributed to the formation of filamentous carbon [6,34,35]. According to Bartholomew [6], this is one of four types of carbon which are formed by the Boudouard reaction {1.7}. Filamentous, or vermicular carbon form at the rear of the metal particle and form a polymeric carbon filament which lifts the metal particle off of the support surface. This continues until the metal particle becomes encapsulated in inactive carbon. This polymeric filament growth exerts pressure on the catalyst support from within the pores. This causes the support to weaken and even break. Bartholomew [6] also points out that the formation of filamentous carbon is retarded and even absent in H_2 rich environments. Since the experimental runs were conducted at low H_2/CO ratios, formation of filamentous carbon on the 70% Ni catalyst was enhanced.

At both 400 and 500°C, the catalyst was operated for 10 hours without severe deactivation (< 10%) and no observable damage to the support. Hayes et al. [35] point out that the formation of carbon on a catalyst surface is initially a slow process, but once started proceeds at a very fast rate. The 10 hour operation time was not long enough to allow the formation of carbon to proceed at a very fast rate. A comparison of the feed and product compositions with the Sigma 115 GC showed no measurable carbon loss. Deactivation required the catalyst to be changed and reduced after three experimental runs. Replacing the catalyst after every three runs insured that the quality of the data would be maintained. All catalyst deactivation was carefully monitored as described in Section 4.2.1.

5.3 Experimental Results

Experimental runs on the 70% Ni catalyst were conducted with steam in the feed at a 1:1 ratio with CO. Experiments without steam were not conducted because of the severe carbon formation on the catalyst in the absence of steam. Experimental runs (Table 3.5)

were conducted at 300°C, 350°C, 400°C, and 500°C. The tabulated results appear in Appendix D. Figures 5.1 to 5.8 show the rate of methanation plotted as a function of H_2 and CO partial pressures. The rate of shift is shown in Figures 5.9 to 5.16.

The data from the experimental runs on the 70% Ni catalyst show trends which are similar to the 0.5% Rh catalyst (Section 4.3). Methanation rates pass through a maximum then decrease and the shifts rate increase with temperature, though not as dramatically as with rhodium. The 70% Ni catalyst has a low selectivity for methane, as evidenced by the higher relative rate of the water-shift reaction.

5.4 Kinetic Expression

A search of the literature produced several studies of nickel catalysts on alumina supports, but as in the case of the 0.5% Rh catalyst, these studies were not conducted at low H_2/CO ratios or in the temperature range of interest. The main reason used by several researchers for not operating below a H_2/CO ratio of three was the formation of carbon on the catalyst. For the sake of comparison a few kinetic expressions for the rate of methanation are presented.

Akers and White [36] conducted a study of methanation kinetics on a nickel kieselguhr catalyst in a temperature range of 300 to 350°C, at H_2/CO ratios between 1.2 and 4. The rate equation which best fit their data was,

$$r = \frac{P_{CO}\, P_{H_2}{}^3}{(A + B\, P_{CO} + D\, P_{CO} + E\, P_{CH_4})^4} \qquad (5.1)$$

where *A,B,D, and E are constants.*

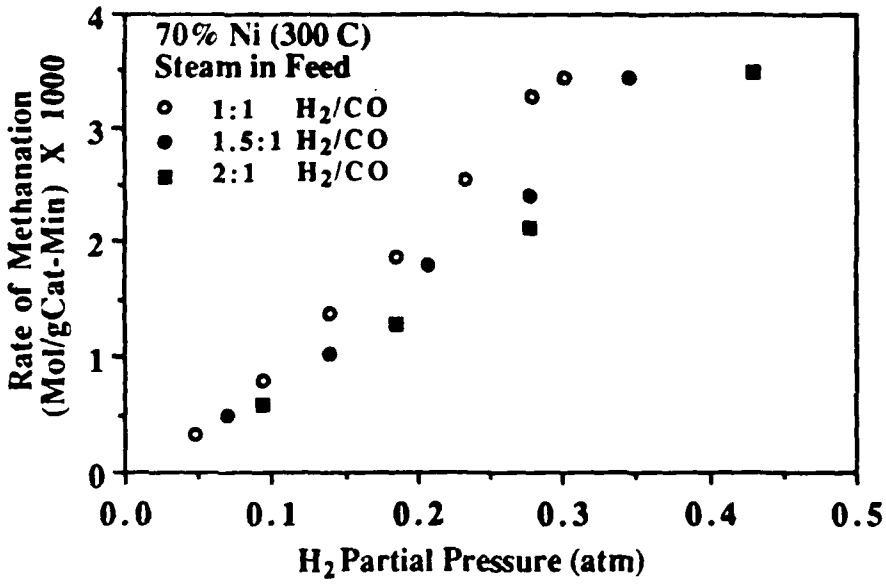


Figure 5.1
Methanation Rate versus H_2 Partial Pressure (300°C)

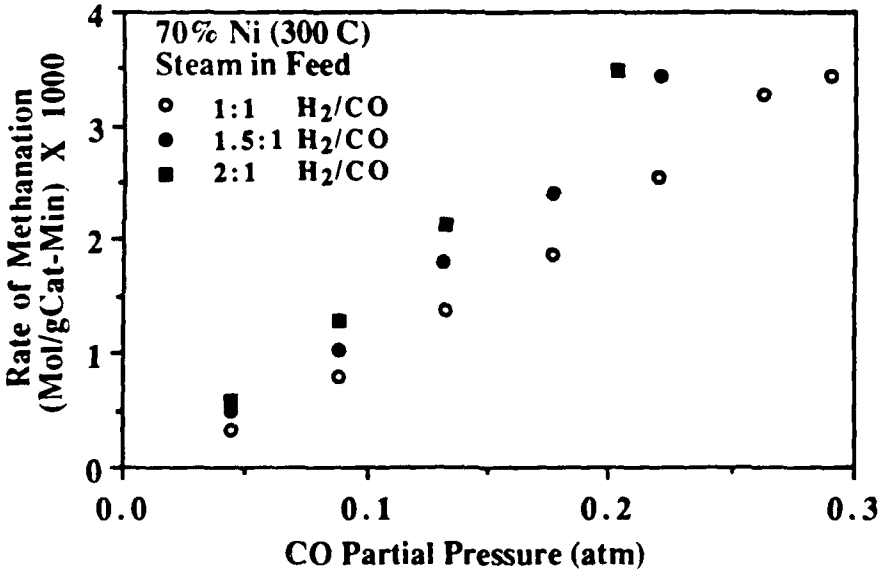


Figure 5.2
Methanation Rate versus CO Partial Pressure (300°C)

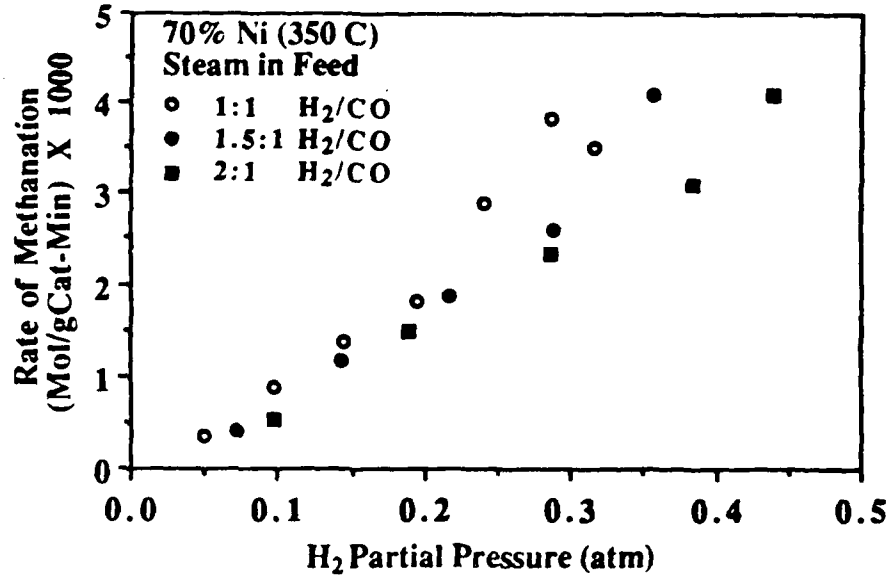


Figure 5.3
Methanation Rate versus H_2 Partial Pressure (350°C)

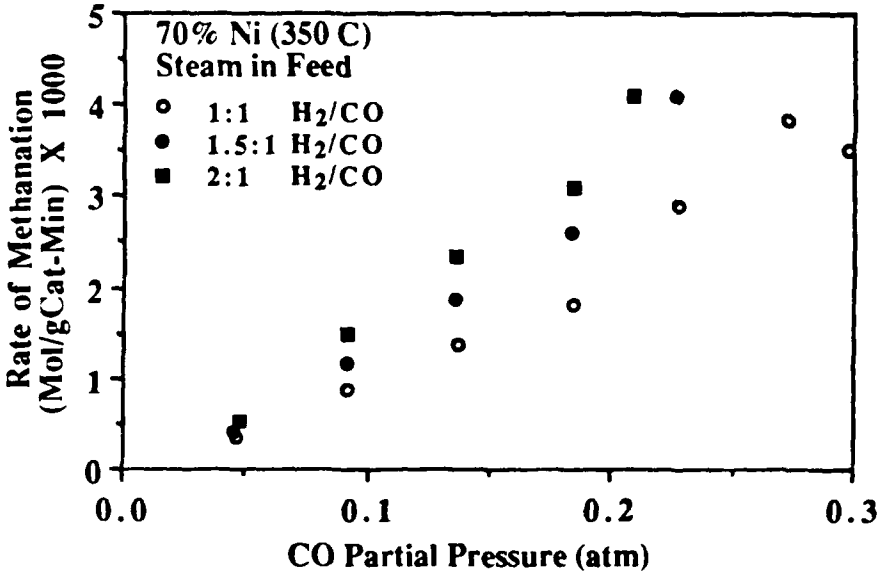


Figure 5.4
Methanation Rate versus CO Partial Pressure (350°C)

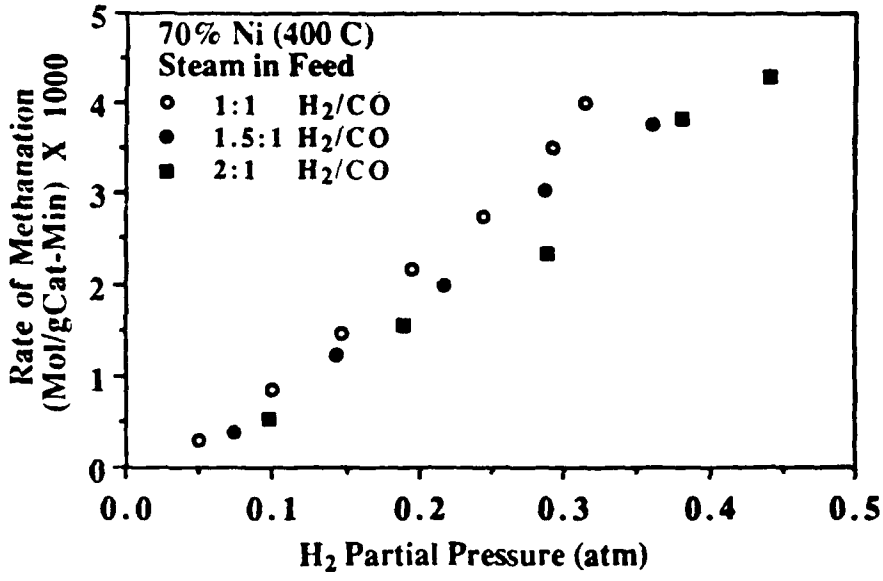


Figure 5.5
Methanation Rate versus H_2 Partial Pressure (400°C)

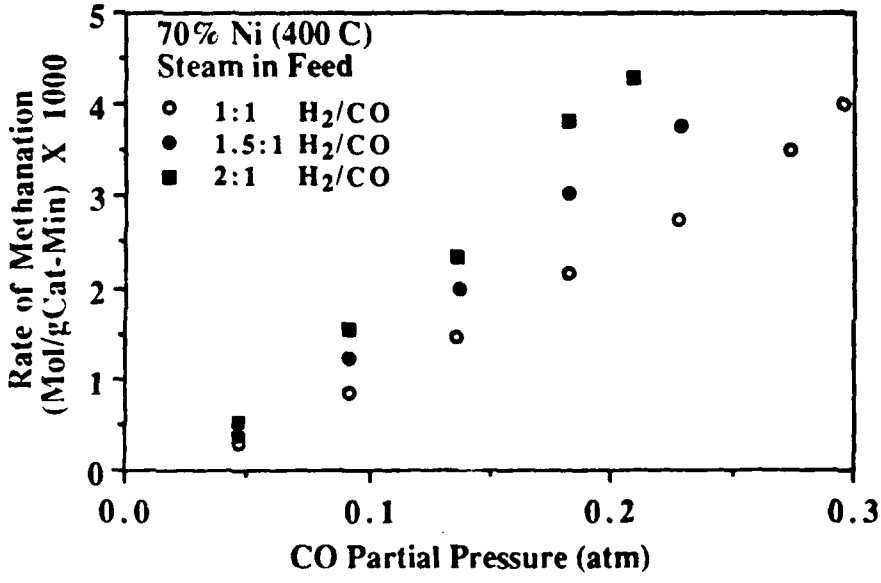


Figure 5.6
Methanation Rate versus CO Partial Pressure (400°C)

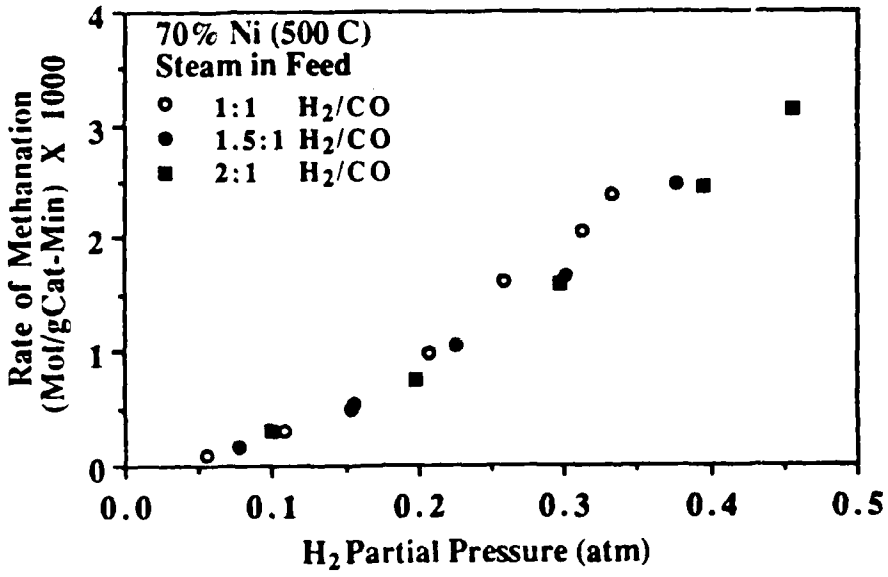


Figure 5.7
Methanation Rate versus H_2 Partial Pressure (500°C)

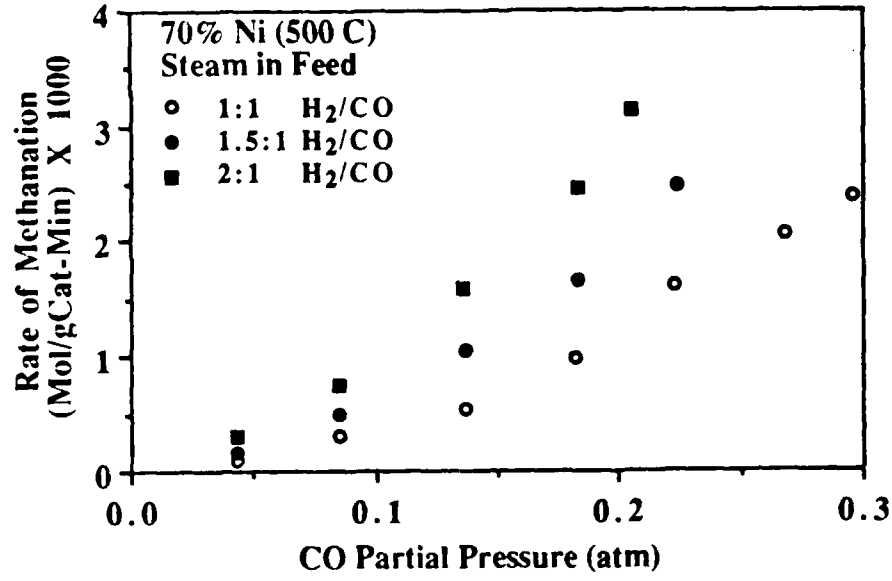


Figure 5.8
Methanation Rate versus CO Partial Pressure (500°C)

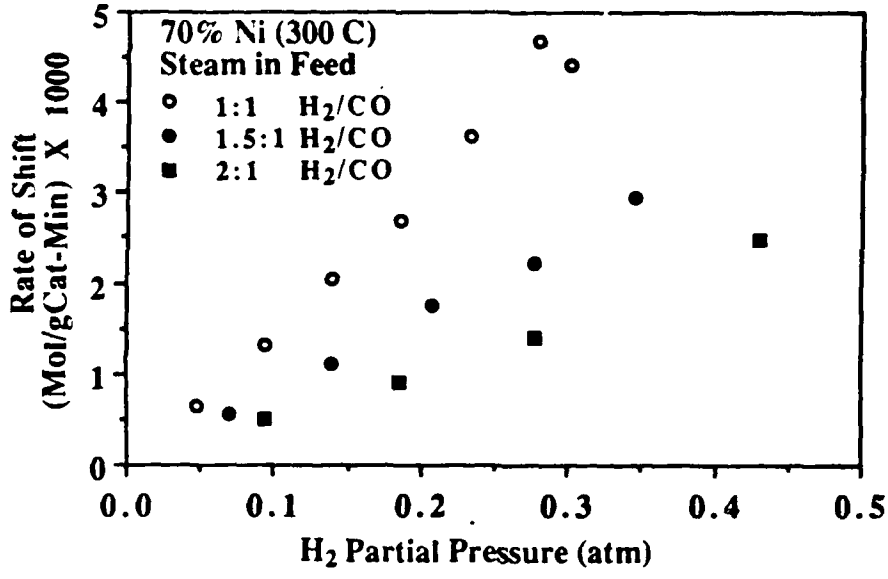


Figure 5.9
Shift Rate versus H_2 Partial Pressure (300°C)

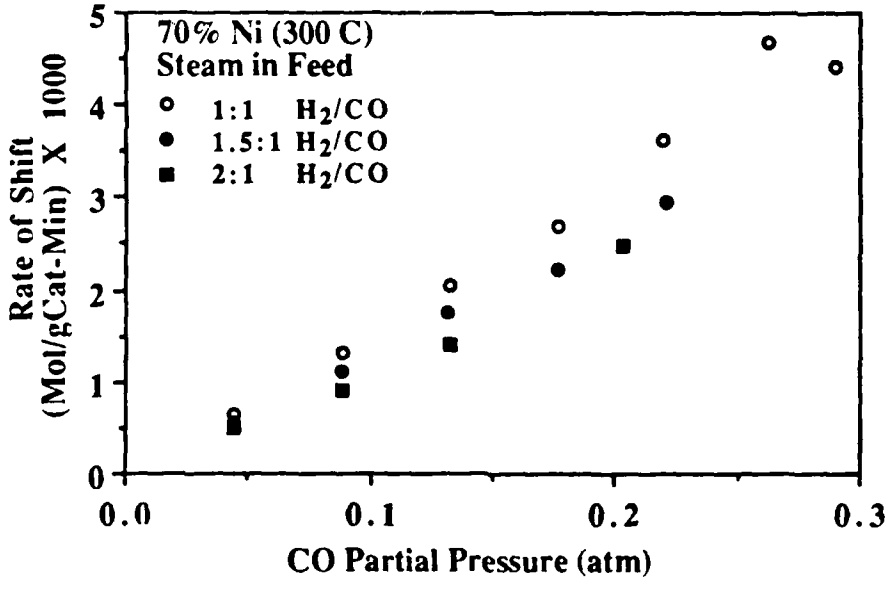


Figure 5.10
Shift Rate versus CO Partial Pressure (300°C)

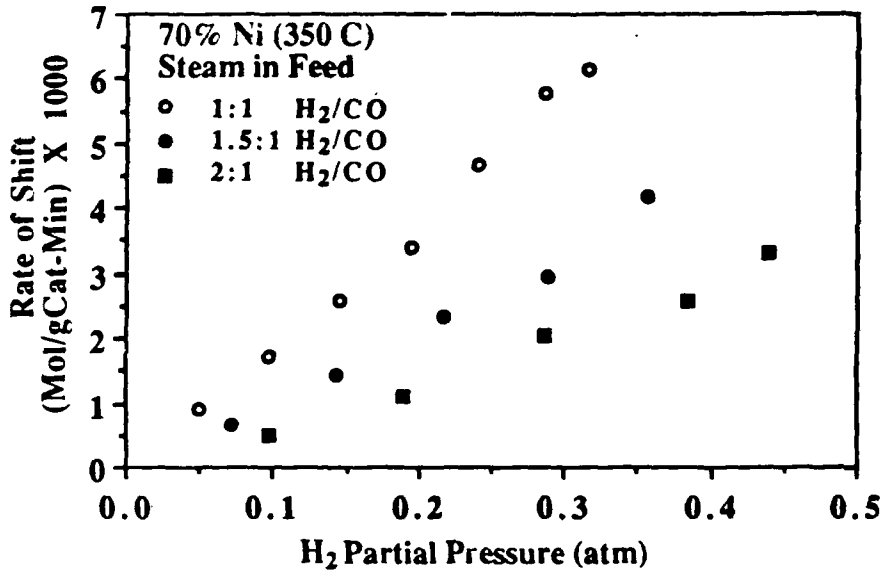


Figure 5.11
Shift Rate versus H_2 Partial Pressure (350°C)

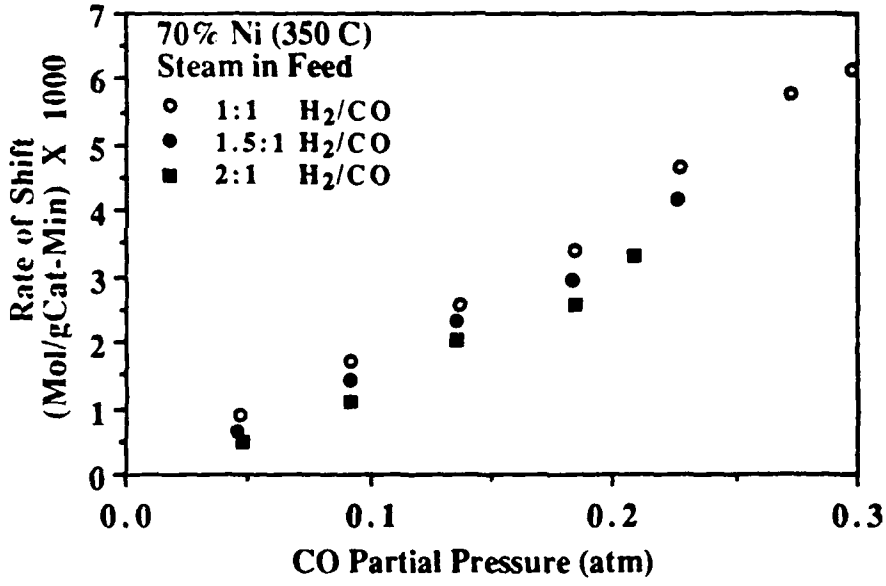


Figure 5.12
Shift Rate versus CO Partial Pressure (350°C)

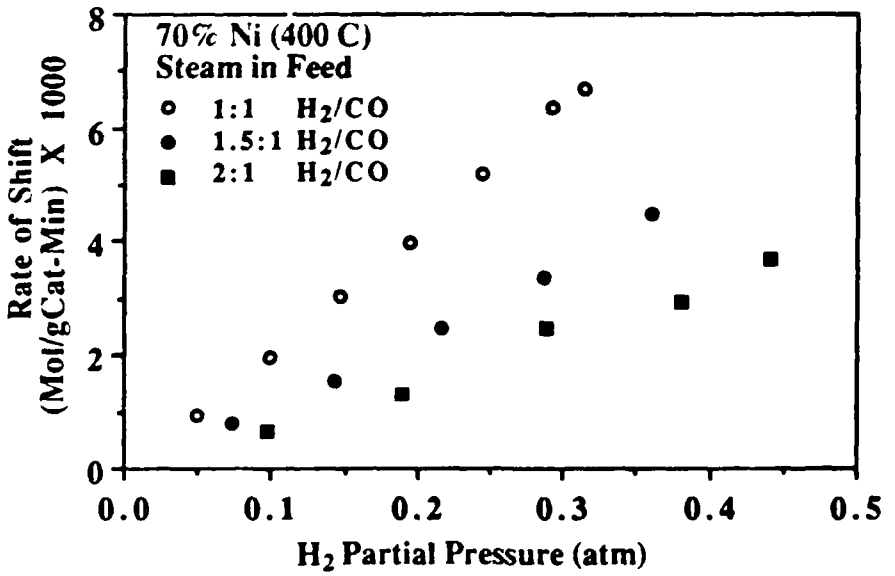


Figure 5.13
Shift Rate versus H_2 Partial Pressure (400°C)

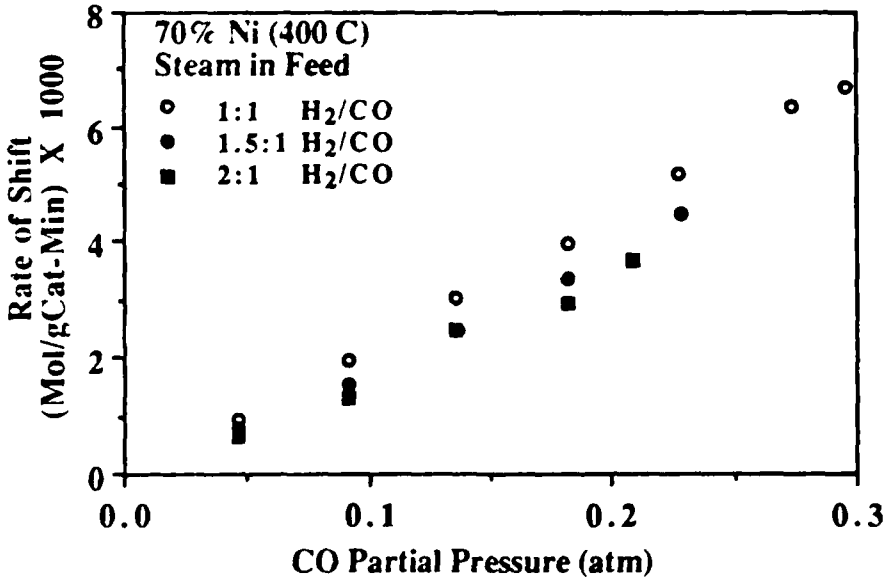


Figure 5.14
Shift Rate versus CO Partial Pressure (400°C)

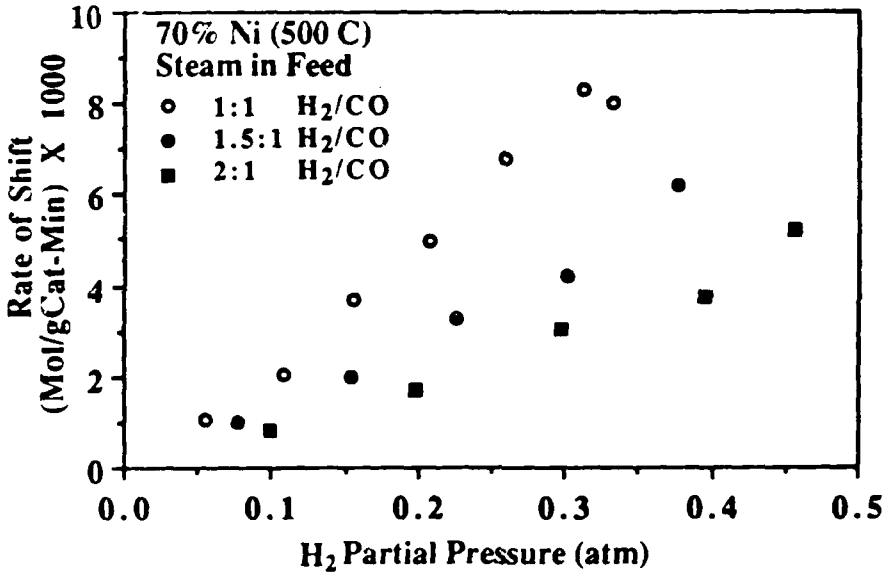


Figure 5.15
Shift Rate versus H_2 Partial Pressure (500°C)

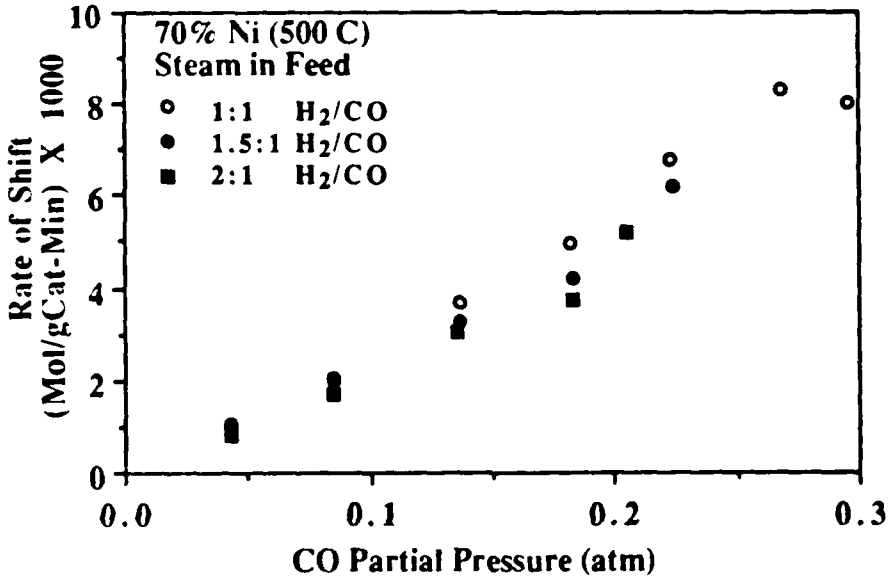


Figure 5.16
Shift Rate versus CO Partial Pressure (500°C)

Lee et al. [37] found a methanation kinetic expression for a nickel catalyst over the 300 tc 450°C temperature range but in a H_2/CO ratio range greater than three. The equation they found to fit their data was,

$$r_{CH_4} = \frac{k\, P_{H_2}^{0.5}\, P_{CO}}{(\,1 + K_2\, P_{H_2} + K_3\, P_{CH_4}\,)} \tag{5.2}$$

The same form of the above expression was found by Bienstock et al. [38] in his work on the synthesis of high Btu gas.

The above expressions were derived from experimental data taken under conditions which were close to the conditions used for the 70% Ni catalyst study, while other work on methanation with nickel catalyst was not. A good summary of this work can be seen in a paper by Vannice [39].

The kinetic expression for the 70% Ni catalyst was developed in the same manner as that of the 0.5% Rh catalyst, with the final form determined by Richardson [16]. A Langmuir-Hinshelwood expression, similar to the one found for the 0.5% Rh catalyst, was fit to the data. The methanation rate fit the equation,

$$\vec{R}_M = \frac{k_M\, K_{CO}\, K_{H_2}\, P_{CO}\, P_{H_2}}{(1 + K_{CO}\, P_{CO} + K_{H_2}\, P_{H_2})} \tag{5.3}$$

with,

$$k_M = 20.9\, e^{-44135/RT} \tag{5.4}$$

$$K_{CO} = 1.01\, e^{12694/RT} \tag{5.5}$$

$$K_{H_2} = 2.41 \times 10^{-4}\, e^{51822/RT}. \tag{5.6}$$

The rate of shift fit

$$\vec{R}_S = k_S\, P_{H_2O} \tag{5.7}$$

$$k_S = 0.168\, e^{-12156/RT} \tag{5.8}$$

with all P's in atmospheres and R = 8.314 J $mole^{-1}K^{-1}$.

These rate equations apply in the temperature range of 300 to 500°C. These equations were found to fit the data fairly well. Tables 5.1 and 5.2 show a comparison of the calculated and experimental rates

Table 5.1

Comparison of Calculated Methanation Rate to Experimental Results

Temperature (°C)	P_{H_2}	P_{CO}	k_M	K_{CO}	K_{H_2}	Rate x 10^3 Calculated	Rate x 10^3 Experimental
300	0.186	0.177	0.00198	14.496	12.736	2.03	1.88
300	0.140	0.132	0.00198	14.496	12.736	1.44	1.37
350	0.195	0.184	0.00417	11.706	5.322	2.21	1.81
350	0.286	0.136	0.00417	11.706	5.322	2.46	2.33
400	0.194	0.182	0.00786	9.758	2.532	2.09	2.16
400	0.147	0.136	0.00786	9.758	2.532	1.44	1.46
500	0.208	0.057	0.02180	7.277	0.764	0.91	0.98
500	0.455	0.205	0.02180	7.277	0.764	3.98	3.14

Table 5.2

Comparison of Calculated Shift Rate to Experimental Results

Temperature (°C)	P_{H_2O}	k_S	Rate x 10^3 Calculated	Rate x 10^3 Experimental
300	0.200	0.013	2.60	1.88
300	0.148	0.013	1.92	2.06
350	0.197	0.016	3.15	3.39
350	0.154	0.016	2.46	2.03
400	0.197	0.019	3.74	3.98
400	0.146	0.019	2.77	3.04
500	0.188	0.025	4.70	4.97
500	0.228	0.025	5.70	5.22

5.5 Kinetic Expressions at High Conversions

As for the 0.5% Rh catalyst, the kinetic expression for the 70% Ni catalyst needed to be modified to account for higher concentrations of products at high conversions. This adjustment was treated in the same manner as for the rhodium catalyst (Section 4.6). The rate of methanation and the rate of shift for the high conversion experiments fit

$$R_M = \frac{k_M K_{H_2} K_{CO} P_{H_2} P_{CO} \left[1 - \frac{P_{CH_4} P_{H_2O}}{K_M P_{CO} P_{H_2}^3}\right]}{(1 + K_{H_2} P_{H_2} + K_{CO} P_{CO} + K_{MP} P_{CH_4} + K_{MP} P_{CO_2})} \qquad (5.9)$$

$$R_S = \frac{k_S P_{H_2O} \left[1 - \frac{P_{CO_2} P_{H_2}}{K_S P_{CO} P_{H_2O}}\right]}{(1 + K_{SP} P_{CH_4} + K_{SP} P_{CO_2})} \qquad (5.10)$$

with the additional constants,

$$K_{MP} = 5.59 \times 10^{-3} e^{26414/RT} \qquad (5.11)$$

$$K_{SP} = 7.75 e^{6345/RT}. \qquad (5.12)$$

Equations 5.9 and 5.10 give an empirical fit over a narrow range of temperature. It is important to point out that these equations apply only from 300 to 350°C which is the practical operating range of this catalyst.

5.6 Lifetime Study

The 70% Ni catalyst was tested with three lifetime studies at 300, 350, and 400°C to check the durability and resistance to carbon formation. Representative data from these studies appears in Appendix F.

The first study at was conducted at 300°C. The reactor was loaded with 6.0425g of 70% Ni catalyst, reduced for eight hours as described in Section 3.4, and run for 300 hours with a feed flow of 400 sccm composed of 28.5% H_2, 19% CO, 19% CO_2, 9.5% CH_4, 19% H_2O, and 5% N_2. The reactor operated at a CO conversion of about 87% for 300 hours with little deactivation (Figure 5.17). Examination of the catalyst revealed no carbon formation or damage to the alumina support.

The second lifetime study was conducted at 400°C. The reactor was loaded with 5.3017g of catalyst, reduced, and run for 300 hours with the same feed mixture used at 300°C. The reactor operated at about 80% CO conversion for 300 hours with little deactivation (Figure 5.19). Examination of the catalyst revealed a thin layer of filamentous carbon on the surface of the pellets. The pellets were also brittle. This test revealed that the 70% Ni catalyst could not be used at 400°C even at low CO partial pressures.

The last lifetime study was conducted at 350°C. This study would reveal if the 70% Ni catalyst can be used between 300 and 350°C. The reactor was loaded with 4.4609g of catalyst, reduced, and run for 300 hours with the same feed mixture used at 300°C. The reactor operated at a CO conversion of about 86% for 300 hours with little deactivation (Figure 5.18). Examination of the catalyst revealed no carbon formation or damage to the support.

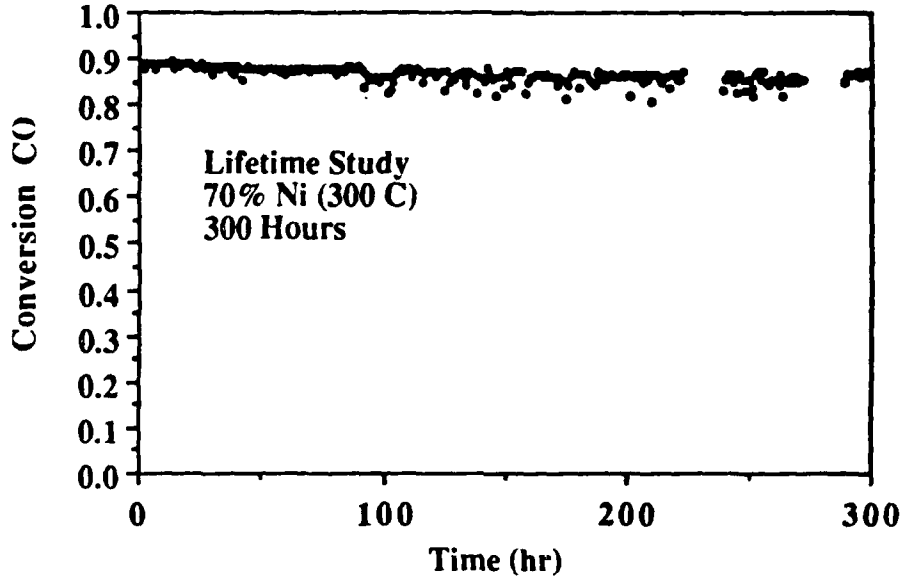


Figure 5.17
Lifetime Study 300°C

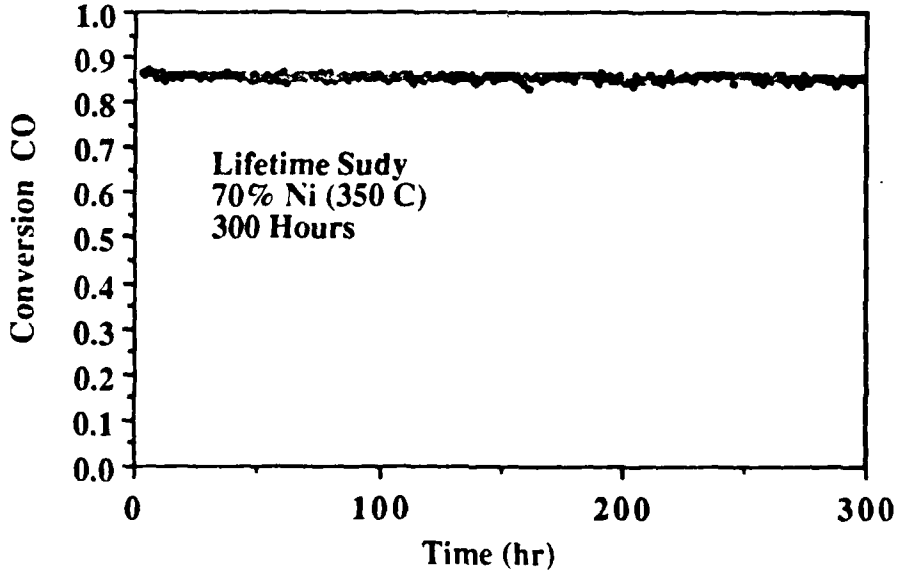


Figure 5.18
Lifetime Study 350°C

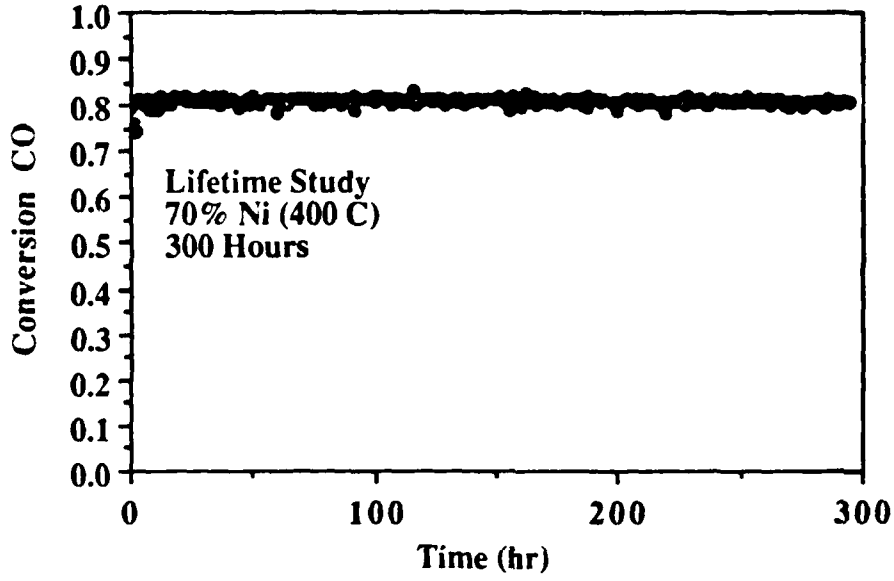


Figure 5.19
Lifetime Study 400°C

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

This study investigated the kinetics of the methanation reaction on 0.5% Rh and 70% Ni catalysts under conditions where the hydrogen to carbon monoxide ratio is near one. The kinetic expressions for both the methanation and shift reactions were developed. The expressions for the 0.5% Rh catalyst are applicable in the range of 400 to 500°C and those for 70% Ni in the 300 to 350°C range. In these ranges the expressions accurately describe the reaction kinetics and will be suitable for reactor design.

The 0.5% Rh catalyst was found suitable for use in the exothermic portion of Chemical Energy Transmission Systems (CETS), which use CO_2 reforming of methane for the endothermic reaction. The catalyst has a high activity at temperatures above 400°C with a high selectivity for methane. Lifetime studies demonstrated the durability of this catalyst at 400°C, and showed no deactivation which could not be attributed to iron impurities in the feed or alumina support.

70% Ni is well suited for low temperature methanation at H_2/CO ratios near one. Nickel has a higher activity and is cheaper than rhodium. This makes it ideal for use in a low temperature isothermal reactor, to complete conversion, in the methanation section of a solar based CETS. The durability and resistance to carbon formation of the 70% Ni catalyst were shown in lifetime studies at 300 and 350°C.

Further studies on the 0.5% Rh catalyst may provide insight into the interaction of steam in the reaction mechanism, and allow the determination of a single expression to describe the reaction kinetics.

The isothermal CSTR was shown to give accurate data which is easy to analyze. Its use reduced the number of assumptions which must be made, thus reducing inaccuracy in the kinetic expressions.

Use of copper and copper alloys, which do not contain catalytic metals, in the construction of the reactor and tubing prevented the formation of coke at H_2/CO ratios near one. This eliminated experimental error due to loss of carbon to coke formation. Aluminum Silicon Bronze (CDA #642) was the alloy used in the CSTR.

Dual element thermocouples allow temperature measurements to be made, for both temperature controllers and the process control computer, at the same location using only one probe. They allow independent operation, free of electrical interference which is caused when two instruments share a common probe.

If the CSTR is to be used for studies at total flow rates higher than 400 sccm, mass flow controllers with a higher flow capacity will be needed.

An Analog Output Card for the MACSYM 2, to control the mass flow controllers, would allow for complete automation of the Catalyst Screening Unit.

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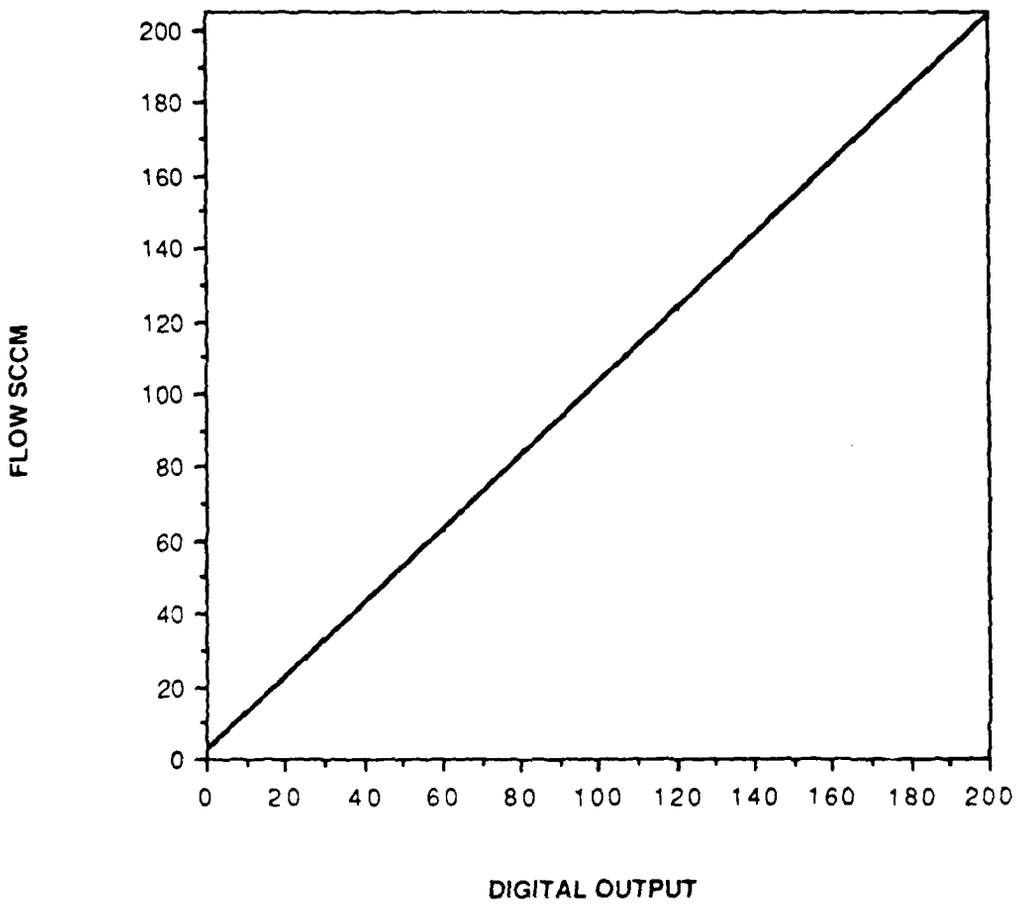
APPENDIX A

CALIBRATION CURVES

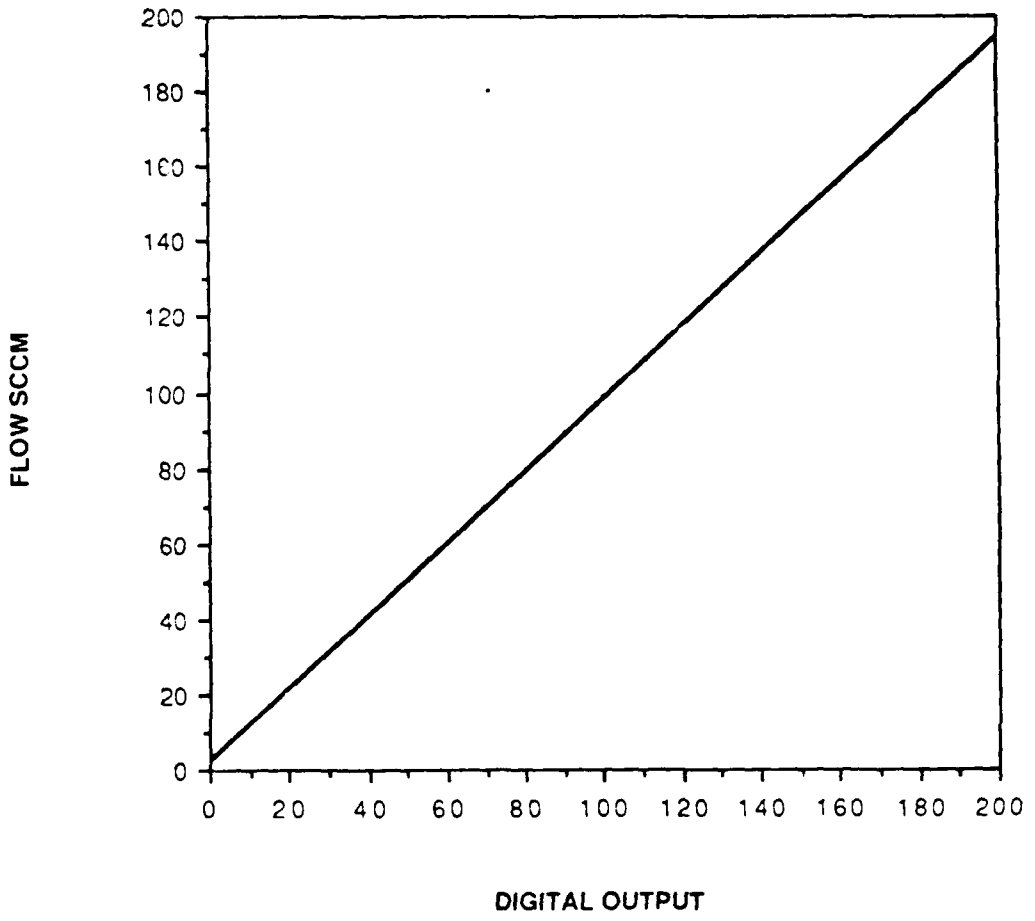
APPENDIX A.1

MASS FLOW CONTROLLER CALIBRATION CURVES

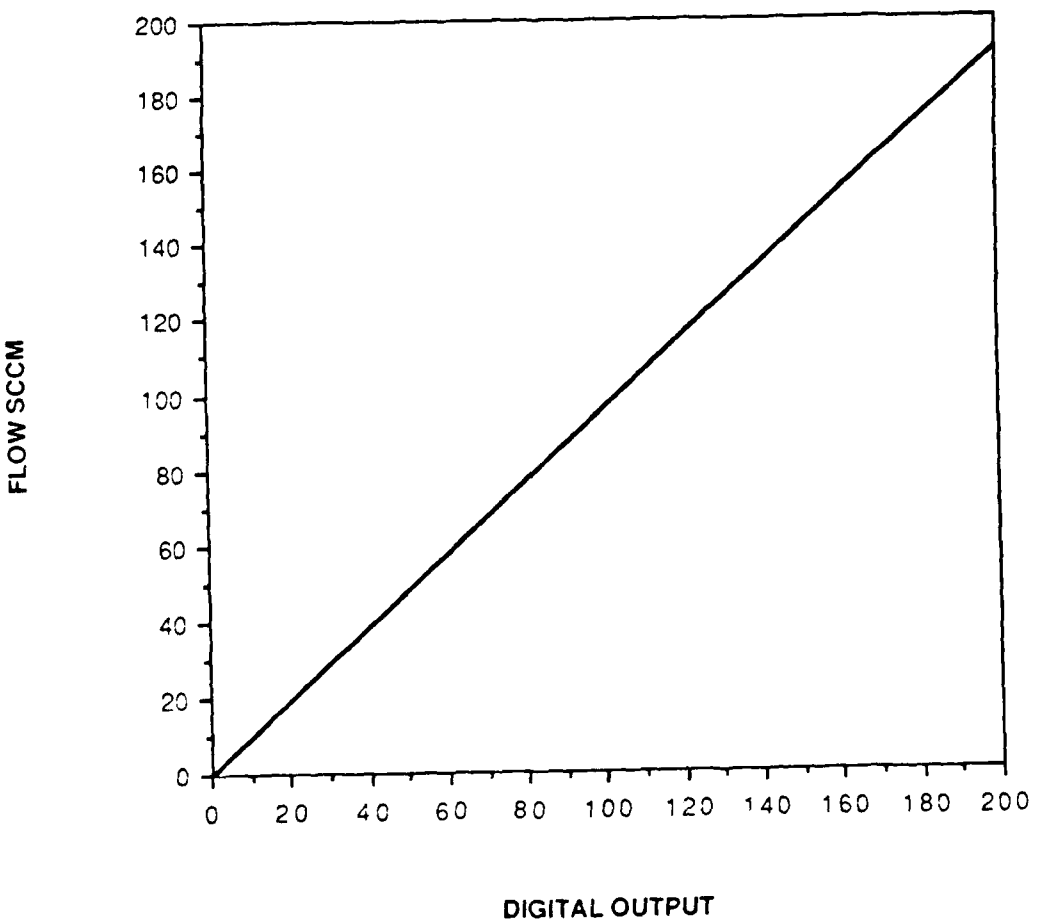
CALIBRATION CURVE HYDROGEN



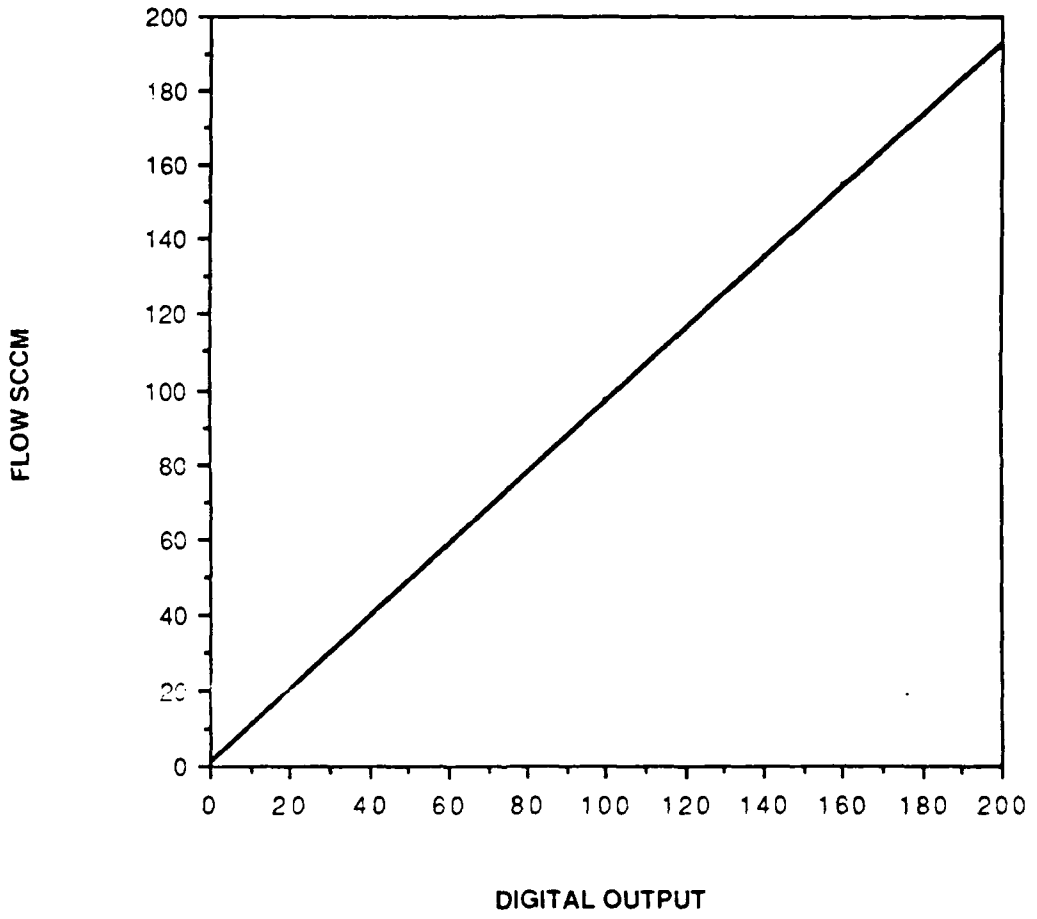
CALIBRATION CURVE HYDROGEN AUX.



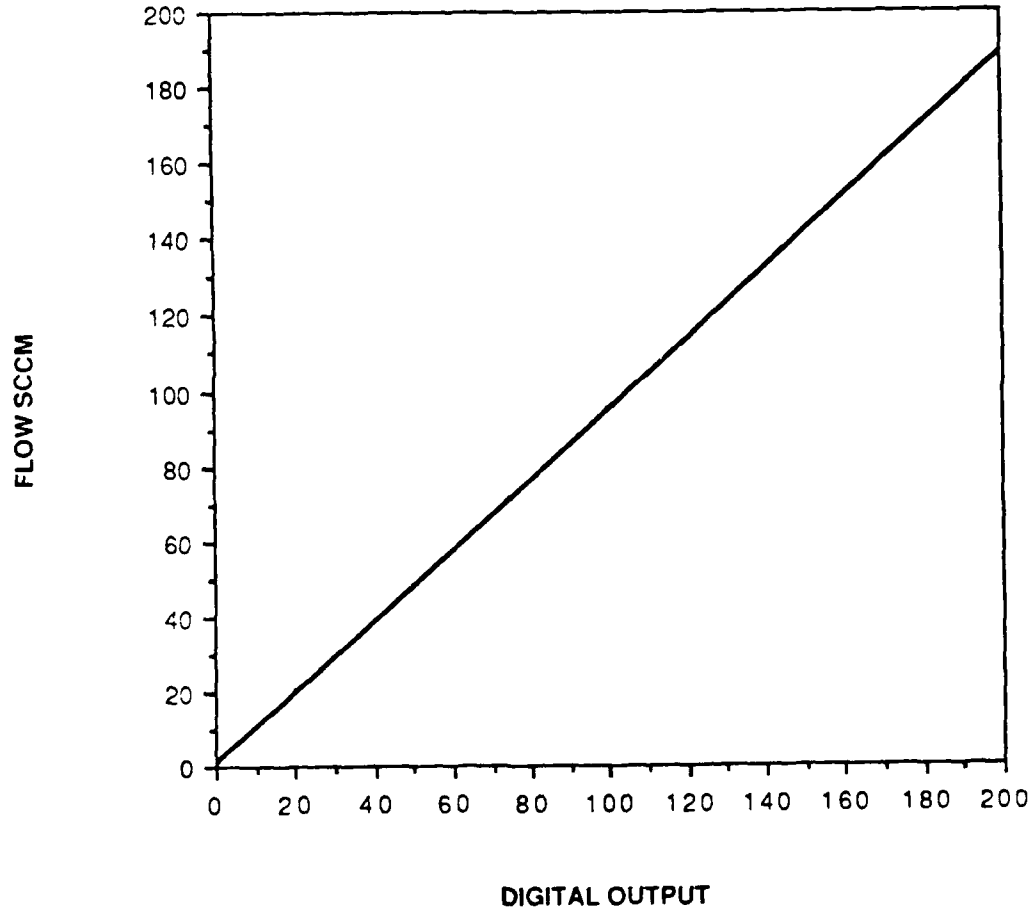
CALIBRATION CURVE NITROGEN



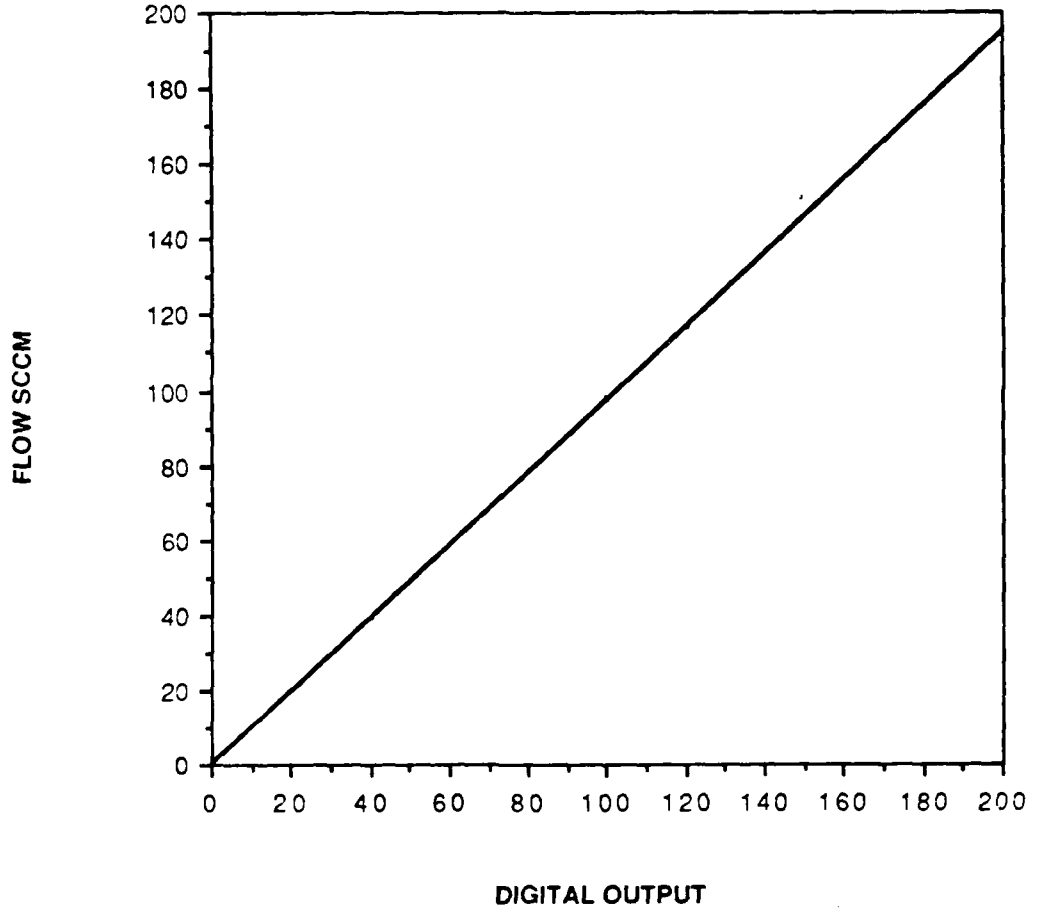
CALIBRATION CURVE NITROGEN AUX.



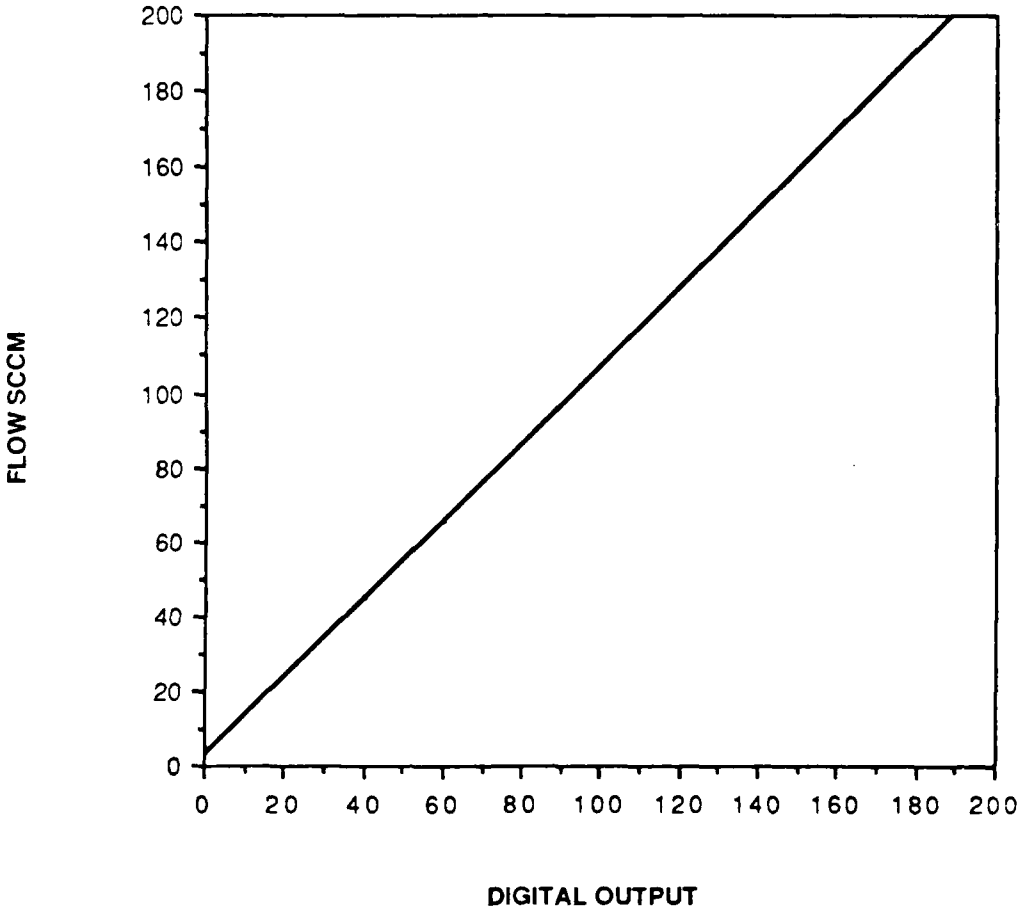
CALIBRATION CURVE CARBON DIOXIDE



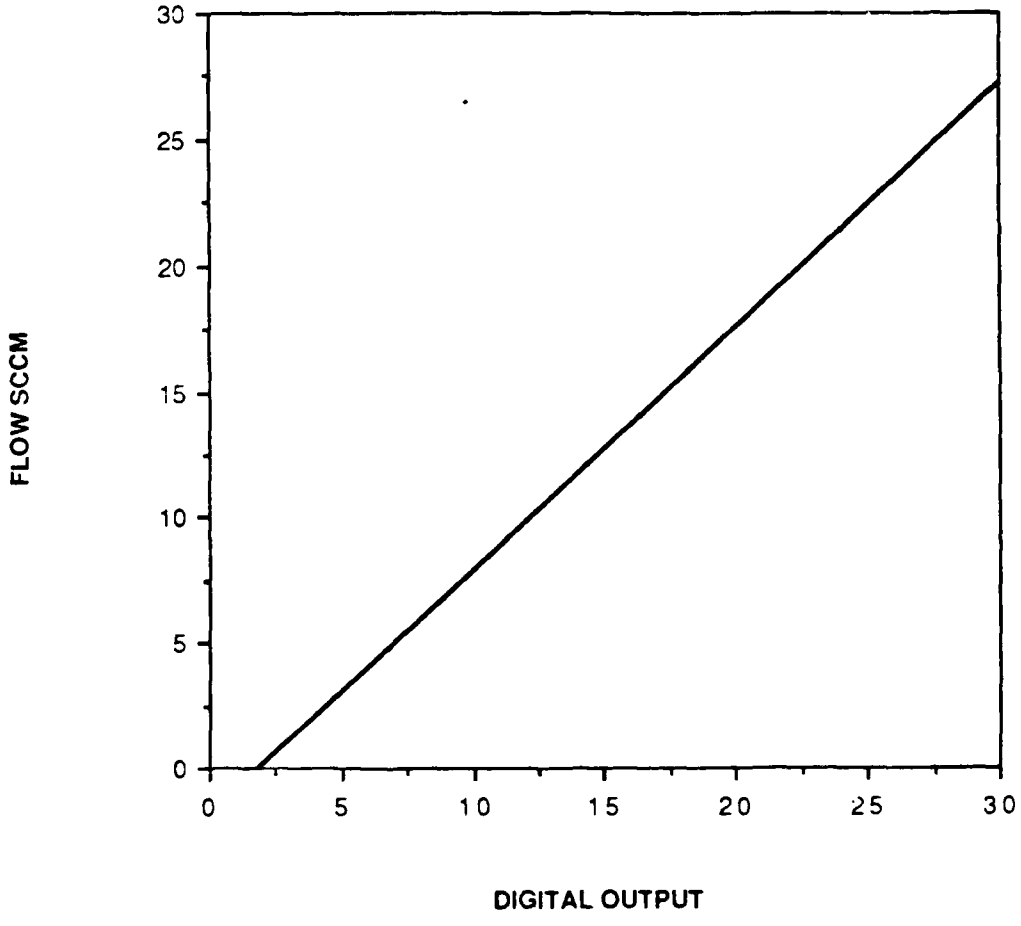
CALIBRATION CURVE CARBON MONOXIDE



CALIBRATION CURVE METHANE



CALIBRATION CURVE FEED SAMPLE



APPENDIX A.2

SYRINGE PUMP CALIBRATION CURVE

Appendix A.2

Conversion of Water to Steam

Feed: Deionized water (23°C, 1 atm)

Product: Steam (105°C, 1 atm)

1g Water (23°C, 1 atm) = 1.00244 cc

1.00244 cc Water (23°C, 1 atm) = 104343 cc Water (100°C, 1 atm)

At 100°C, 1 atm: 1.04343 cc Water = 1672.24 cc Steam

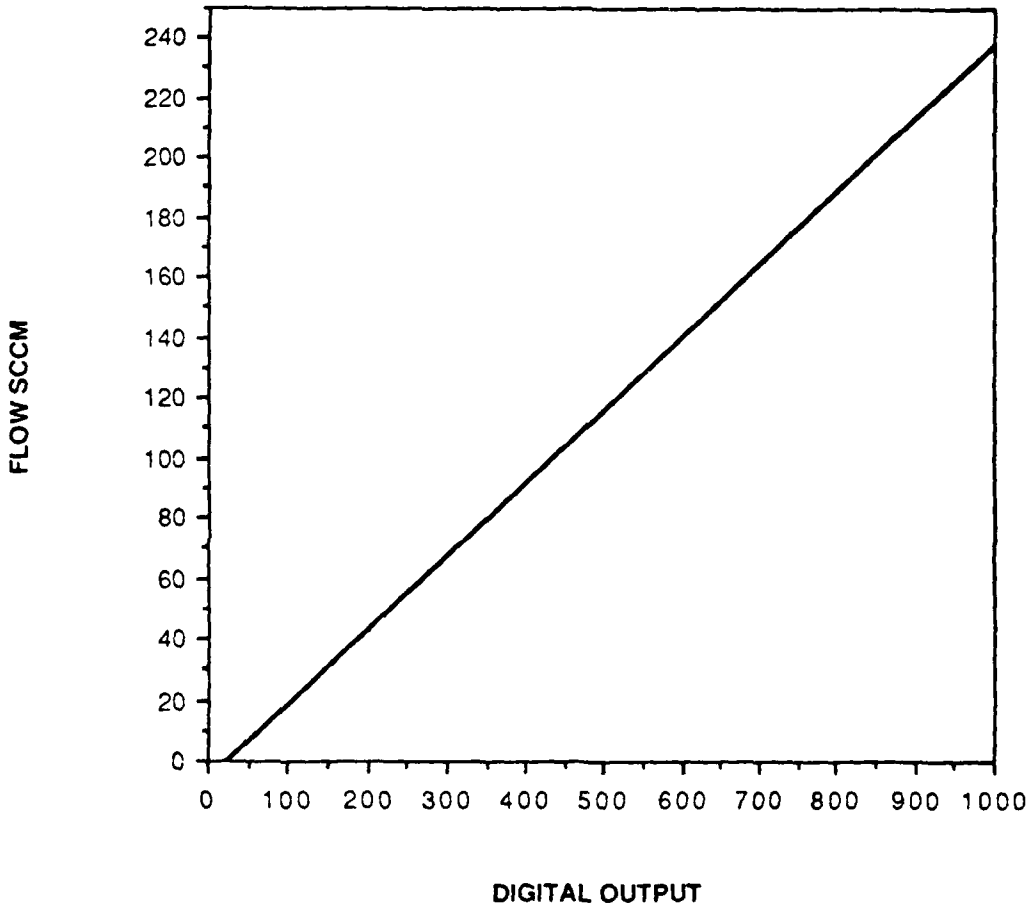
1672.24 cc Steam (100°C, 1 atm) = 1694.65 cc Steam (105°C, 1 atm)

Using the Ideal Gas Law

1694.65 cc Steam (105°C, 1 atm) = 1224.1 cc Steam (0°C, 1 atm)

1g Water (23°C, 1 atm) = 1224.1 cc Steam (0°C, 1 atm)

CALIBRATION CURVE SYRINGE PUMP



APPENDIX B

CHROMATOGRAPHIC METHOD

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METHOD   1

ANALYZER CONTROL

INJ TEMP      150
DET ZONE 1,2      150    150
AUX TEMP       25
FLOW A,B      30    30
INIT OVEN TEMP,TIME      100    17

DATA PROC

STD WT,SMP WT       0.0000      1.0000  0
FACTOR,SCALE          1    0
TIMES      17.00      0.00  327.67  327.67  327.67  327.67
SENS-DET RANGE      100      8      0.00      2    0    0
UNK,AIR      0.000      0.00
TOL         0.0500    0.200       2.0
REF PK       1.000      3.00      3.25      3.15
STD NAME   CARBON MONOXIDE

   RT       RF        CONC      NAME
    1.50   32.000   100.0000 HYDROGEN
    2.60    0.498   100.0000 NITROGEN
    3.15    0.500   100.0000 CARBON MONOXIDE
    5.00    0.595   100.0000 METHANE
   12.50    0.426   100.0000 CARBON DIOXIDE

EVENT CONTROL

ATTN-CHART-DELAY        6     5     0.01

   TIME  DEVICE      FUNCTION NAME
    0.10 EXT     X   -7        POL REV
    0.11 ZERO    Z    1        SET ZERO
    2.00 EXT     X    7        NORM ZERO
    2.02 ZERO    Z    1        SET ZERO
```

APPENDIX C

EXPERIMENTAL RUN DATA 0.5% Rh CATALYST

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	1	2	3	4	5
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	.075	.075	.075	.075	.075
FEED RATE (SCCM)	382	382	382	380	380
CONVERSION CO	.127	.09	.052	.115	.086
YIELD OF CH4	.114	.078	.045	.108	.074
RATE METH. x 1000 (MOL/gCAT-MIN)	6.465	4.443	2.534	4.896	3.336
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.761	.642	.42	.298	.561
FEED PARTIAL PRESSURES (ATM)					
H2	.5	.375	.25	.4	.3
CO	.25	.25	.25	.2	.2
N2	.25	.375	.5	.4	.5
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.443	.332	.223	.352	.266
CO	.231	.237	.242	.185	.188
N2	.265	.39	.511	.418	.515
CH4	.03	.02	.011	.023	.015
CO2	.004	.003	.002	.001	.003
H2O	.027	.017	.01	.021	.013
CORRECTION FACTOR	1	1	1	.982	.964

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	6	7	8	9	10
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	.075	.075	.075	.075	.075
FEED RATE (SCCM)	380	380	380	380	380
CONVERSION CO	.051	.106	.082	.05	.136
YIELD OF CH4	.043	.095	.07	.042	.122
RATE METH. x 1000 (MOL/gCAT-MIN)	1.921	3.204	2.37	1.417	8.253
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.393	.4	.393	.285	.956
FEED PARTIAL PRESSURES (ATM)					
H2	.2	.3	.225	.15	.6
CO	.2	.15	.15	.15	.3
N2	.6	.55	.625	.7	.1
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.179	.267	.199	.134	.534
CO	.193	.138	.141	.144	.28
N2	.61	.566	.638	.709	.108
CH4	.009	.015	.011	.006	.039
CO2	.002	.002	.002	.001	.005
H2O	.007	.013	.009	.005	.035
CORRECTION FACTOR	.947	.9	.882	.865	.853

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	11	12	13	14	15
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	.075	.075	.075	.075	.075
FEED RATE (SCCM)	380	380	380	380	380
CONVERSION CO	.098	.059	.106	.111	.058
YIELD OF CH4	.084	.049	.092	.096	.049
RATE METH. x 1000 (MOL/gCAT-MIN)	5.71	3.336	7.255	8.428	3.853
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.936	.637	1.116	1.384	.767
FEED PARTIAL PRESSURES (ATM)					
H2	.45	.3	.525	.585	.35
CO	.3	.3	.35	.39	.35
N2	.25	.4	.125	.025	.3
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.398	.266	.463	.518	.313
CO	.285	.291	.334	.375	.341
N2	.263	.412	.134	.027	.311
CH4	.027	.015	.034	.04	.018
CO2	.004	.003	.005	.007	.004
H2O	.022	.012	.029	.034	.014
CORRECTION FACTOR	.835	.817	.781	.77	.759

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	16	17	18	19	20
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	.075	.075	.075	.179	.179
FEED RATE (SCCM)	380	380	380	379	379
CONVERSION CO	.061	.06	.06	.185	.14
YIELD OF CH4	.052	.051	.052	.159	.112
RATE METH. x 1000 (MOL/gCAT-MIN)	4.62	5.043	5.715	1.497	1.055
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.785	.875	.919	.247	.264
FEED PARTIAL PRESSURES (ATM)					
H2	.39	.44	.49	.2	.15
CO	.39	.44	.49	.1	.1
N2	.22	.12	.02	.7	.75
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.346	.395	.44	.16	.122
CO	.382	.433	.485	.084	.088
N2	.229	.126	.021	.723	.767
CH4	.021	.023	.027	.016	.011
CO2	.004	.004	.004	.003	.003
H2O	.018	.019	.022	.014	.009
CORRECTION FACTOR	.721	.7	.678	.986	.973

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	21	22	23	24	25
TEMPERATURE (C)	400	400	400	400	350
CATALYST WEIGHT (gr)	.179	.179	.179	.179	.471
FEED RATE (SCCM)	379	379	379	379	383
CONVERSION CO	.097	.154	.126	.087	.078
YIELD OF CH4	.073	.123	.093	.057	.072
RATE METH. x 1000 (MOL/gCAT-MIN)	.686	.582	.438	.269	.657
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.231	.146	.158	.14	.048
FEED PARTIAL PRESSURES (ATM)					
H2	.1	.1	.075	.05	.5
CO	.1	.05	.05	.05	.25
N2	.8	.85	.875	.9	.25
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.082	.084	.063	.043	.464
CO	.092	.043	.044	.046	.239
N2	.812	.861	.883	.905	.259
CH4	.007	.006	.005	.003	.019
CO2	.002	.002	.002	.001	.001
H2O	.005	.005	.003	.001	.017
CORRECTION FACTOR	.96	.91	.895	.88	1

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	26	27	28	29	30
TEMPERATURE (C)	350	350	350	350	350
CATALYST WEIGHT (gr)	.471	.471	.193	.193	.193
FEED RATE (SCCM)	383	382	391	391	391
CONVERSION CO	.072	.084	.134	.16	.178
YIELD OF CH4	.069	.078	.128	.154	.174
RATE METH. x 1000 (MOL/gCAT-MIN)	.752	.563	2.286	2.087	1.574
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.035	.046	.12	.086	.04
FEED PARTIAL PRESSURES (ATM)					
H2	.6	.4	.79	.6	.4
CO	.3	.2	.198	.15	.1
N2	.1	.4	.013	.25	.5
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.562	.366	.754	.558	.361
CO	.29	.189	.18	.132	.085
N2	.104	.413	.013	.262	.518
CH4	.022	.016	.027	.024	.018
CO2	.001	.001	.001	.001	0
H2O	.021	.015	.025	.023	.018
CORRECTION FACTOR	.988	.976	.911	.968	.937

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	31	32	33	36	37
TEMPERATURE (C)	350	350	350	350	350
CATALYST WEIGHT (gr)	.193	.193	.193	.193	.193
FEED RATE (SCCM)	391	391	391	390	390
CONVERSION CO	.085	.093	.173	.116	.127
YIELD OF CH4	.079	.084	.155	.108	.117
RATE METH. x 1000 (MOL/gCAT-MIN)	1.747	1.526	.704	1.463	1.053
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.144	.163	.078	.113	.091
FEED PARTIAL PRESSURES (ATM)					
H2	.735	.6	.2	.45	.3
CO	.245	.2	.05	.15	.1
N2	.02	.2	.75	.4	.6
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.706	.57	.18	.416	.272
CO	.233	.188	.042	.137	.089
N2	.021	.207	.762	.413	.614
CH4	.02	.017	.008	.017	.012
CO2	.002	.002	.001	.001	.001
H2O	.018	.016	.007	.015	.011
CORRECTION FACTOR	.884	.841	.806	.956	.915

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	38	39	40	41	42
TEMPERATURE (C)	350	450	450	450	450
CATALYST WEIGHT (gr)	.193	.096	.096	.096	.096
FEED RATE (SCCM)	390	389	389	389	388
CONVERSION CO	.134	.139	.12	.146	.119
YIELD OF CH4	.118	.118	.103	.132	.098
RATE METH. x 1000 (MOL/gCAT-MIN)	.533	5.322	3.721	7.185	2.645
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.073	.992	.638	.745	.572
FEED PARTIAL PRESSURES (ATM)					
H2	.15	.5	.4	.6	.3
CO	.05	.25	.2	.3	.15
N2	.8	.25	.4	.1	.55
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.135	.443	.357	.527	.267
CO	.044	.229	.183	.278	.136
N2	.81	.266	.417	.109	.567
CH4	.006	.031	.021	.043	.015
CO2	.001	.006	.004	.004	.003
H2O	.005	.025	.018	.039	.012
CORRECTION FACTOR	.878	1	.974	.931	.864

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	43	44	45	46	47
TEMPERATURE (C)	450	450	450	450	450
CATALYST WEIGHT (gr)	.096	.096	.096	.096	.096
FEED RATE (SCCM)	388	387	388	389	389
CONVERSION CO	.099	.077	.112	.114	.12
YIELD OF CH4	.078	.058	.081	.089	.094
RATE METH. x 1000 (MOL/gCAT-MIN)	1.404	.522	2.942	4.035	5.098
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.388	.174	1.109	1.141	1.44
FEED PARTIAL PRESSURES (ATM)					
H2	.2	.1	.3	.375	.45
CO	.1	.05	.2	.25	.3
N2	.7	.85	.5	.375	.25
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.182	.093	.266	.329	.396
CO	.092	.046	.184	.232	.28
N2	.711	.855	.517	.392	.265
CH4	.008	.003	.017	.023	.03
CO2	.002	.001	.006	.007	.008
H2O	.006	.002	.01	.017	.021
CORRECTION FACTOR	.857	.85	.833	.822	.81

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	48	49	50	51	52
TEMPERATURE (C)	450	450	450	450	450
CATALYST WEIGHT (gr)	.096	.096	.096	.096	.096
FEED RATE (SCCM)	389	388	388	389	389
CONVERSION CO	.128	.081	.086	.091	.134
YIELD OF CH4	.1	.054	.059	.063	.106
RATE METH. x 1000 (MOL/gCAT-MIN)	6.353	1.944	2.643	3.424	7.468
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.744	.979	1.256	1.5	2.007
FEED PARTIAL PRESSURES (ATM)					
H2	.525	.2	.25	.3	.585
CO	.35	.2	.25	.3	.39
N2	.125	.6	.5	.4	.025
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.462	.177	.219	.261	.515
CO	.328	.188	.235	.284	.368
N2	.134	.613	.515	.416	.027
CH4	.038	.011	.015	.02	.045
CO2	.01	.006	.007	.009	.012
H2O	.027	.005	.008	.011	.033
CORRECTION FACTOR	.8	.78	.767	.755	.743

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	53	54	55	56	57
TEMPERATURE (C)	450	450	450	450	450
CATALYST WEIGHT (gr)	.096	.096	.096	.096	.144
FEED RATE (SCCM)	389	389	389	389	388
CONVERSION CO	.095	.092	.098	.097	.147
YIELD OF CH4	.065	.065	.068	.069	.105
RATE METH. x 1000 (MOL/gCAT-MIN)	4.096	4.614	5.42	6.107	1.891
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.902	1.915	2.407	2.521	.761
FEED PARTIAL PRESSURES (ATM)					
H2	.35	.39	.44	.49	.225
CO	.35	.39	.44	.49	.15
N2	.3	.22	.12	.02	.625
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.307	.342	.387	.432	.19
CO	.332	.373	.422	.474	.132
N2	.314	.232	.128	.021	.645
CH4	.024	.027	.032	.036	.016
CO2	.011	.011	.014	.015	.007
H2O	.013	.016	.018	.021	.01
CORRECTION FACTOR	.754	.747	.74	.735	.976

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	58	59	60	61	62
TEMPERATURE (C)	450	450	450	450	450
CATALYST WEIGHT (gr)	.144	.144	.144	.144	.144
FEED RATE (SCCM)	388	388	388	388	388
CONVERSION CO	.131	.102	.079	.099	.116
YIELD OF CH4	.09	.068	.04	.061	.076
RATE METH. x 1000 (MOL/gCAT-MIN)	1.09	.409	.242	.731	1.381
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.487	.207	.234	.463	.716
FEED PARTIAL PRESSURES (ATM)					
H2	.15	.075	.05	.1	.15
CO	.1	.05	.05	.1	.15
N2	.75	.875	.9	.8	.7
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.129	.067	.046	.087	.124
CO	.089	.045	.046	.091	.136
N2	.764	.881	.904	.81	.716
CH4	.009	.003	.002	.006	.012
CO2	.004	.002	.002	.004	.006
H2O	.005	.002	0	.002	.006
CORRECTION FACTOR	.953	.931	.91	.891	.872

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	63	64	65	66	67
TEMPERATURE (C)	500	500	500	500	500
CATALYST WEIGHT (gr)	.1	.1	.1	.1	.1
FEED RATE (SCCM)	389	389	389	388	388
CONVERSION CO	.12	.102	.122	.096	.099
YIELD OF CH4	.089	.074	.086	.067	.073
RATE METH. x 1000 (MOL/gCAT-MIN)	3.886	2.587	4.512	2.904	2.542
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.345	.947	1.864	1.241	.879
FEED PARTIAL PRESSURES (ATM)					
H2	.5	.4	.6	.375	.3
CO	.25	.2	.3	.25	.2
N2	.25	.4	.1	.375	.5
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.461	.372	.562	.343	.269
CO	.23	.185	.278	.234	.186
N2	.262	.412	.105	.388	.515
CH4	.023	.015	.027	.017	.015
CO2	.008	.006	.011	.007	.005
H2O	.015	.01	.016	.01	.01
CORRECTION FACTOR	1	.916	.846	.572	.586

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	68	69	70	71	72
TEMPERATURE (C)	500	500	500	500	500
CATALYST WEIGHT (gr)	.1	.1	.1	.1	.1
FEED RATE (SCCM)	388	388	388	388	388
CONVERSION CO	.106	.09	.078	.066	.071
YIELD OF CH4	.072	.066	.05	.038	.038
RATE METH. x 1000 (MOL/gCAT-MIN)	3.724	1.715	1.3	.989	1.308
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.771	.629	.739	.733	1.148
FEED PARTIAL PRESSURES (ATM)					
H2	.45	.3	.225	.15	.2
CO	.3	.15	.15	.15	.2
N2	.25	.55	.625	.7	.6
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.414	.28	.21	.139	.187
CO	.28	.139	.14	.142	.189
N2	.261	.561	.634	.708	.609
CH4	.022	.01	.008	.006	.008
CO2	.011	.004	.004	.004	.007
H2O	.012	.006	.003	.001	.001
CORRECTION FACTOR	.573	.908	.831	.767	.595

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	73	74	75	76	77
TEMPERATURE (C)	500	500	500	500	500
CATALYST WEIGHT (gr)	.1	.1	.1	.1	.1
FEED RATE (SCCM)	388	388	389	388	389
CONVERSION CO	.075	.078	.111	.085	.119
YIELD OF CH4	.048	.051	.08	.053	.084
RATE METH. x 1000 (MOL/gCAT-MIN)	2.075	2.667	4.872	3.197	5.707
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.17	1.378	1.917	1.955	2.374
FEED PARTIAL PRESSURES (ATM)					
H2	.25	.3	.525	.35	.585
CO	.25	.3	.35	.35	.39
N2	.5	.4	.125	.3	.025
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.226	.27	.479	.318	.535
CO	.237	.286	.329	.333	.368
N2	.512	.413	.132	.311	.027
CH4	.012	.016	.03	.019	.035
CO2	.007	.008	.012	.012	.015
H2O	.005	.008	.018	.007	.02
CORRECTION FACTOR	.588	.582	.546	.532	.519

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	78	79	80	81	82
TEMPERATURE (C)	500	500	500	500	500
CATALYST WEIGHT (gr)	.1	.1	.1	.186	.186
FEED RATE (SCCM)	387	387	387	387	387
CONVERSION CO	.09	.082	.08	.114	.087
YIELD OF CH4	.054	.053	.053	.071	.05
RATE METH. x 1000 (MOL/gCAT-MIN)	3.654	4.062	4.472	.33	.233
RATE SHIFT x 1000 (MOL/gCAT-MIN)	2.409	2.207	2.33	.2	.172
FEED PARTIAL PRESSURES (ATM)					
H2	.39	.44	.49	.1	.075
CO	.39	.44	.49	.05	.05
N2	.22	.12	.02	.85	.875
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	0
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.356	.401	.449	.092	.07
CO	.371	.424	.475	.045	.046
N2	.23	.126	.021	.856	.879
CH4	.022	.025	.027	.004	.003
CO2	.014	.013	.014	.002	.002
H2O	.007	.011	.013	.001	.001
CORRECTION FACTOR	.435	.431	.428	.935	.87

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	83	84	85	86	91
TEMPERATURE (C)	500	500	500	500	400
CATALYST WEIGHT (gr)	.186	.186	.186	.186	.147
FEED RATE (SCCM)	387	388	387	387	400
CONVERSION CO	.067	.153	.135	.101	.129
YIELD OF CH4	.038	.109	.092	.056	.108
RATE METH. x 1000 (MOL/gCAT-MIN)	.175	1.014	.849	.515	2.62
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.134	.409	.408	.419	.516
FEED PARTIAL PRESSURES (ATM)					
H2	.05	.2	.15	.1	.4
CO	.05	.1	.1	.1	.2
N2	.9	.7	.75	.8	.2
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	0	0	0	0	.2
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.046	.176	.129	.089	.355
CO	.047	.087	.088	.091	.182
N2	.903	.716	.764	.809	.209
CH4	.002	.011	.009	.006	.022
CO2	.001	.004	.004	.005	.004
H2O	0	.007	.005	.001	.227
CORRECTION FACTOR	.805	.68	.674	.653	1

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	92	93	94	95	96
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	.147	.147	.147	.147	.147
FEED RATE (SCCM)	400	400	400	400	400
CONVERSION CO	.087	.058	.116	.076	.052
YIELD OF CH4	.069	.039	.092	.065	.03
RATE METH. x 1000 (MOL/gCAT-MIN)	1.677	.95	1.682	1.191	.553
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.446	.453	.427	.194	.4
FEED PARTIAL PRESSURES (ATM)					
H2	.3	.2	.3	.225	.15
CO	.2	.2	.15	.15	.15
N2	.3	.4	.4	.475	.55
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.2	.2	.15	.15	.15
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.27	.183	.27	.201	.141
CO	.188	.191	.136	.141	.143
N2	.309	.406	.411	.484	.555
CH4	.014	.008	.014	.01	.005
CO2	.004	.004	.004	.002	.003
H2O	.216	.207	.165	.161	.153
CORRECTION FACTOR	.978	.958	.945	.93	.916

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	97	98	99	100	101
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	.147	.147	.147	.147	.147
FEED RATE (SCCM)	391	391	391	391	391
CONVERSION CO	.135	.074	.052	.049	.051
YIELD OF CH4	.114	.057	.035	.034	.037
RATE METH. x 1000 (MOL/gCAT-MIN)	3.125	1.708	1.038	1.217	1.431
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.569	.497	.515	.535	.557
FEED PARTIAL PRESSURES (ATM)					
H2	.46	.375	.25	.3	.325
CO	.23	.25	.25	.3	.325
N2	.08	.125	.25	.1	.025
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.23	.25	.25	.3	.325
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.407	.346	.232	.28	.301
CO	.21	.238	.241	.291	.316
N2	.084	.129	.254	.102	.026
CH4	.028	.015	.009	.01	.012
CO2	.005	.004	.004	.005	.005
H2O	.265	.268	.259	.312	.341
CORRECTION FACTOR	.895	.872	.849	.816	.78

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	102	103	104	105	106
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	.241	.241	.241	.241	.241
FEED RATE (SCCM)	391	391	391	391	391
CONVERSION CO	.147	.136	.099	.188	.14
YIELD OF CH4	.096	.082	.036	.14	.095
RATE METH. x 1000 (MOL/gCAT-MIN)	.349	.296	.131	1.012	.689
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.184	.197	.229	.349	.323
FEED PARTIAL PRESSURES (ATM)					
H2	.1	.075	.05	.2	.15
CO	.05	.05	.05	.1	.1
N2	.8	.825	.85	.6	.65
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.05	.05	.05	.1	.1
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.089	.066	.048	.168	.128
CO	.043	.044	.045	.084	.088
N2	.808	.832	.853	.617	.663
CH4	.005	.004	.002	.014	.01
CO2	.003	.003	.003	.005	.005
H2O	.053	.052	.049	.112	.107
CORRECTION FACTOR	.986	.972	.959	.945	.933

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	107	108	109	110	111
TEMPERATURE (C)	400	450	450	450	450
CATALYST WEIGHT (gr)	.241	.095	.095	.095	.095
FEED RATE (SCCM)	391	391	391	391	390
CONVERSION CO	.1	.138	.123	.096	.132
YIELD OF CH4	.05	.092	.069	.04	.085
RATE METH. x 1000 (MOL/gCAT-MIN)	.359	3.375	2.518	1.463	2.349
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.367	1.702	1.993	2.059	1.29
FEED PARTIAL PRESSURES (ATM)					
H2	.1	.4	.3	.2	.3
CO	.1	.2	.2	.2	.15
N2	.7	.2	.3	.4	.4
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.1	.2	.2	.2	.15
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.091	.368	.277	.19	.276
CO	.091	.179	.18	.184	.134
N2	.707	.208	.308	.406	.411
CH4	.005	.019	.014	.008	.013
CO2	.005	.01	.011	.011	.007
H2O	.101	.217	.209	.2	.16
CORRECTION FACTOR	.92	1	1	1	.964

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	112	113	114	115	116
TEMPERATURE (C)	450	450	450	450	450
CATALYST WEIGHT (gr)	.095	.095	.095	.095	.095
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.11	.092	.133	.114	.101
YIELD OF CH4	.059	.035	.089	.066	.043
RATE METH. x 1000 (MOL/gCAT-MIN)	1.617	.963	3.736	3.016	1.976
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.419	1.557	1.881	2.205	2.649
FEED PARTIAL PRESSURES (ATM)					
H2	.225	.15	.46	.375	.25
CO	.15	.15	.23	.25	.25
N2	.475	.55	.08	.125	.25
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.15	.15	.23	.25	.25
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.21	.144	.427	.349	.237
CO	.136	.138	.208	.229	.23
N2	.484	.556	.083	.129	.256
CH4	.009	.005	.021	.017	.011
CO2	.008	.009	.011	.012	.015
H2O	.154	.148	.25	.263	.252
CORRECTION FACTOR	.955	.945	.996	.993	.894

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	117	118	119	120	121
TEMPERATURE (C)	450	450	450	450	450
CATALYST WEIGHT (gr)	.095	.095	.191	.191	.191
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.097	.104	.187	.156	.144
YIELD OF CH4	.043	.051	.088	.058	.035
RATE METH. x 1000 (MOL/gCAT-MIN)	2.354	3.063	.399	.264	.161
RATE SHIFT x 1000 (MOL/gCAT-MIN)	2.954	3.152	.452	.448	.494
FEED PARTIAL PRESSURES (ATM)					
H2	.3	.325	.1	.075	.05
CO	.3	.325	.05	.05	.05
N2	.1	.025	.8	.825	.85
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.3	.325	.05	.05	.05
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.285	.302	.093	.072	.05
CO	.278	.301	.041	.042	.043
N2	.103	.026	.807	.83	.853
CH4	.013	.017	.004	.003	.002
CO2	.017	.018	.005	.005	.005
H2O	.305	.336	.05	.048	.047
CORRECTION FACTOR	.887	.88	1	1	1

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	122	123	124	125	126
TEMPERATURE (C)	450	450	450	500	500
CATALYST WEIGHT (gr)	.191	.191	.191	.095	.095
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.199	.174	.153	.139	.123
YIELD OF CH4	.117	.079	.045	.074	.05
RATE METH. x 1000 (MOL/gCAT-MIN)	1.071	.723	.408	2.681	1.806
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.74	.863	.983	2.386	2.674
FEED PARTIAL PRESSURES (ATM)					
H2	.2	.15	.1	.4	.3
CO	.1	.1	.1	.2	.2
N2	.6	.65	.7	.2	.3
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.1	.1	.1	.2	.2
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.177	.138	.098	.38	.291
CO	.082	.084	.086	.177	.179
N2	.614	.66	.706	.206	.306
CH4	.012	.008	.005	.015	.01
CO2	.008	.01	.011	.013	.015
H2O	.106	.1	.095	.208	.199
CORRECTION FACTOR	.98	.98	.93	1	.994

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	127	128	129	130	131
TEMPERATURE (C)	500	500	500	500	500
CATALYST WEIGHT (gr)	.095	.095	.095	.095	.095
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.11	.128	.121	.11	.15
YIELD OF CH4	.029	.063	.043	.023	.086
RATE METH. x 1000 (MOL/gCAT-MIN)	1.069	1.735	1.165	.629	3.608
RATE SHIFT x 1000 (MOL/gCAT-MIN)	2.929	1.756	2.137	2.369	2.668
FEED PARTIAL PRESSURES (ATM)					
H2	.2	.3	.225	.15	.46
CO	.2	.15	.15	.15	.23
N2	.4	.4	.475	.55	.08
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.2	.15	.15	.15	.23
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.201	.287	.22	.154	.432
CO	.18	.133	.134	.134	.204
N2	.405	.408	.481	.554	.083
CH4	.006	.01	.006	.003	.021
CO2	.016	.01	.012	.013	.015
H2O	.192	.153	.147	.141	.245
CORRECTION FACTOR	.989	.923	.914	.904	.88

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	132	133	134	135	136
TEMPERATURE (C)	500	500	500	500	500
CATALYST WEIGHT (gr)	.095	.095	.095	.095	.193
FEED RATE (SCCM)	390	390	388	388	390
CONVERSION CO	.129	.121	.112	.125	.175
YIELD OF CH4	.057	.035	.038	.042	.039
RATE METH. x 1000 (MOL/gCAT-MIN)	2.599	1.596	2.079	2.447	.176
RATE SHIFT x 1000 (MOL/gCAT-MIN)	3.297	3.899	3.99	4.906	.611
FEED PARTIAL PRESSURES (ATM)					
H2	.375	.25	.3	.325	.1
CO	.25	.25	.3	.325	.05
N2	.125	.25	.1	.025	.8
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.25	.25	.3	.325	.05
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.361	.249	.294	.32	.101
CO	.224	.224	.273	.292	.041
N2	.129	.254	.102	.026	.803
CH4	.015	.009	.012	.014	.002
CO2	.019	.022	.023	.028	.007
H2O	.253	.242	.296	.32	.045
CORRECTION FACTOR	.896	.895	.906	.905	.975

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	137	138	139	140	141
TEMPERATURE (C)	500	500	500	500	500
CATALYST WEIGHT (gr)	.193	.193	.193	.193	.193
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.162	.181	.219	.194	.188
YIELD OF CH4	.032	.017	.087	.058	.042
RATE METH. x 1000 (MOL/gCAT-MIN)	.142	.075	.78	.524	.375
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.586	.738	1.187	1.223	1.321
FEED PARTIAL PRESSURES (ATM)					
H2	.075	.05	.2	.15	.1
CO	.05	.05	.1	.1	.1
N2	.825	.85	.6	.65	.7
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.05	.05	.1	.1	.1
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.077	.056	.191	.148	.103
CO	.042	.041	.08	.082	.082
N2	.828	.851	.611	.658	.706
CH4	.002	.001	.009	.006	.004
CO2	.007	.008	.013	.014	.015
H2O	.045	.043	.097	.093	.09
CORRECTION FACTOR	.952	.929	.905	.905	.905

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	142	143	144	145	146
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	1.528	1.528	1.528	1.528	1.528
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.346	.308	.281	.593	.599
YIELD OF CH4	.194	.185	.176	.427	.426
RATE METH. x 1000 (MOL/gCAT-MIN)	.441	.525	.602	.973	.728
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.348	.351	.357	.377	.295
FEED PARTIAL PRESSURES (ATM)					
H2	.2	.25	.3	.4	.3
CO	.2	.25	.3	.2	.15
N2	.4	.25	.1	.2	.4
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.2	.25	.3	.2	.15
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.124	.157	.193	.213	.154
CO	.142	.191	.241	.098	.069
N2	.434	.275	.112	.241	.459
CH4	.042	.051	.059	.103	.073
CO2	.033	.034	.035	.04	.03
H2O	.226	.292	.36	.304	.216
CORRECTION FACTOR	1	.986	.971	.989	.977

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	147	148	149	150	151
TEMPERATURE (C)	400	400	450	500	450
CATALYST WEIGHT (gr)	1.528	1.528	1.528	1.528	1.526
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.599	.521	.629	.643	.634
YIELD OF CH4	.395	.289	.246	.191	.244
RATE METH. x 1000 (MOL/gCAT-MIN)	.45	.329	.56	.434	.556
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.232	.264	.871	1.031	.89
FEED PARTIAL PRESSURES (ATM)					
H2	.2	.15	.2	.2	.2
CO	.1	.1	.2	.2	.2
N2	.6	.65	.4	.4	.4
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.1	.1	.2	.2	.2
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.111	.092	.143	.191	.146
CO	.043	.051	.082	.077	.081
N2	.652	.69	.444	.433	.443
CH4	.043	.031	.055	.041	.054
CO2	.022	.025	.085	.098	.087
H2O	.129	.112	.192	.16	.189
CORRECTION FACTOR	.992	.947	.954	.89	1

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	152	153	154	155	156
TEMPERATURE (C)	450	450	450	450	450
CATALYST WEIGHT (gr)	1.526	1.526	1.526	1.526	1.526
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.64	.653	.51	.582	.6
YIELD OF CH4	.255	.27	.145	.196	.215
RATE METH. x 1000 (MOL/gCAT-MIN)	.727	.925	.083	.224	.367
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.096	1.309	.208	.44	.66
FEED PARTIAL PRESSURES (ATM)					
H2	.25	.3	.05	.1	.15
CO	.25	.3	.05	.1	.15
N2	.25	.1	.85	.7	.55
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.25	.3	.05	.1	.15
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.178	.205	.047	.083	.119
CO	.103	.124	.025	.043	.064
N2	.287	.119	.863	.729	.588
CH4	.073	.097	.007	.02	.034
CO2	.11	.137	.019	.04	.062
H2O	.249	.318	.04	.084	.133
CORRECTION FACTOR	.996	.992	.979	.976	.974

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	157	158	159	160	161
TEMPERATURE (C)	450	450	450	500	500
CATALYST WEIGHT (gr)	1.526	1.526	1.526	.761	.761
FEED RATE (SCCM)	390	390	390	389	389
CONVERSION CO	.729	.697	.639	.426	.447
YIELD OF CH4	.445	.412	.345	.127	.146
RATE METH. x 1000 (MOL/gCAT-MIN)	1.015	.705	.393	.579	.831
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.648	.488	.336	1.367	1.717
FEED PARTIAL PRESSURES (ATM)					
H2	.4	.3	.2	.2	.25
CO	.2	.15	.1	.2	.25
N2	.2	.4	.6	.4	.25
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.2	.15	.1	.2	.25
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.231	.18	.135	.194	.233
CO	.066	.052	.039	.121	.149
N2	.243	.456	.644	.421	.27
CH4	.108	.071	.037	.027	.039
CO2	.069	.049	.032	.063	.081
H2O	.282	.193	.113	.174	.228
CORRECTION FACTOR	.971	.97	.971	1	.997

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	162	163	164	165	166
TEMPERATURE (C)	500	500	500	500	500
CATALYST WEIGHT (gr)	.761	.761	.761	.761	.761
FEED RATE (SCCM)	389	389	390	390	390
CONVERSION CO	.452	.486	.501	.489	.411
YIELD OF CH4	.158	.252	.232	.17	.08
RATE METH. x 1000 (MOL/gCAT-MIN)	1.078	1.148	.797	.388	.183
RATE SHIFT x 1000 (MOL/gCAT-MIN)	2.018	1.072	.923	.731	.756
FEED PARTIAL PRESSURES (ATM)					
H2	.3	.4	.3	.2	.1
CO	.3	.2	.15	.1	.1
N2	.1	.2	.4	.6	.7
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.3	.2	.15	.1	.1
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.272	.329	.253	.187	.111
CO	.181	.114	.08	.053	.06
N2	.11	.222	.43	.621	.711
CH4	.052	.056	.037	.018	.008
CO2	.098	.052	.043	.033	.034
H2O	.286	.226	.155	.088	.076
CORRECTION FACTOR	.994	.991	.88	.88	.88

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	167	167	167	167	167
TEMPERATURE (C)	500	500	500	500	500
CATALYST WEIGHT (gr)	.761	.761	.761	.761	.761
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.452	.452	.452	.452	.452
YIELD OF CH4	.108	.108	.108	.108	.108
RATE METH. x 1000 (MOL/gCAT-MIN)	.371	.371	.371	.371	.371
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.179	1.179	1.179	1.179	1.179
FEED PARTIAL PRESSURES (ATM)					
H2	.15	.15	.15	.15	.15
CO	.15	.15	.15	.15	.15
N2	.55	.55	.55	.55	.55
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.15	.15	.15	.15	.15
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.158	.158	.158	.158	.158
CO	.085	.085	.085	.085	.085
N2	.568	.568	.568	.568	.568
CH4	.017	.017	.017	.017	.017
CO2	.053	.053	.053	.053	.053
H2O	.119	.119	.119	.119	.119
CORRECTION FACTOR	.88	.88	.88	.88	.88

APPENDIX D

EXPERIMENTAL RUN DATA 70% Ni CATALYST

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	1	2	3	4	5
TEMPERATURE (C)	300	300	300	300	300
CATALYST WEIGHT (gr)	.105	.105	.105	.105	.105
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.137	.14	.137	.118	.125
YIELD OF CH4	.057	.073	.085	.041	.06
RATE METH. x 1000 (MOL/gCAT-MIN)	1.881	2.42	2.835	.338	.494
RATE SHIFT x 1000 (MOL/gCAT-MIN)	2.682	2.23	1.732	.641	.547
FEED PARTIAL PRESSURES (ATM)					
H2	.2	.3	.2	.05	.075
CO	.2	.2	.2	.05	.05
N2	.4	.3	.4	.85	.825
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.2	.2	.2	.05	.05
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.186	.278	.165	.048	.07
CO	.177	.177	.179	.044	.044
N2	.409	.309	.414	.853	.83
CH4	.012	.015	.018	.002	.003
CO2	.017	.014	.011	.004	.003
H2O	.2	.207	.214	.048	.05
CORRECTION FACTOR	1	1	1	.985	.97

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	6	7	8	9	10
TEMPERATURE (C)	300	300	300	300	300
CATALYST WEIGHT (gr)	.105	.105	.105	.105	.105
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.131	.127	.129	.131	.138
YIELD OF CH4	.071	.048	.062	.077	.055
RATE METH. x 1000 (MOL/gCAT-MIN)	.588	.803	1.034	1.28	1.369
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.496	1.315	1.112	.896	2.059
FEED PARTIAL PRESSURES (ATM)					
H2	.1	.1	.15	.2	.15
CO	.05	.1	.1	.1	.15
N2	.8	.7	.65	.6	.55
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.05	.1	.1	.1	.15
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.093	.094	.14	.185	.14
CO	.044	.088	.088	.088	.132
N2	.806	.707	.658	.609	.559
CH4	.004	.005	.006	.008	.008
CO2	.003	.008	.007	.005	.013
H2O	.051	.098	.101	.104	.148
CORRECTION FACTOR	.955	.995	.991	.986	.996

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	11	12	13	14	15
TEMPERATURE (C)	300	300	300	300	300
CATALYST WEIGHT (gr)	.105	.105	.105	.105	.105
FEED RATE (SCCM)	390	390	389	389	390
CONVERSION CO	.142	.141	.154	.149	.157
YIELD OF CH4	.072	.085	.083	.062	.092
RATE METH. x 1000 (MOL/gCAT-MIN)	1.79	2.124	3.431	2.561	3.497
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.757	1.391	2.967	3.614	2.488
FEED PARTIAL PRESSURES (ATM)					
H2	.225	.3	.375	.25	.46
CO	.15	.15	.25	.25	.23
N2	.475	.4	.125	.25	.08
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.15	.15	.25	.25	.23
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.208	.277	.345	.233	.43
CO	.131	.132	.221	.22	.203
N2	.485	.41	.13	.258	.084
CH4	.011	.013	.022	.016	.022
CO2	.011	.009	.019	.022	.016
H2O	.154	.158	.264	.251	.246
CORRECTION FACTOR	.992	.988	.983	.966	1

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	16	17	18	19	20
TEMPERATURE (C)	300	300	400	400	400
CATALYST WEIGHT (gr)	.105	.105	.06	.06	.06
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.16	.145	.105	.109	.116
YIELD OF CH4	.066	.064	.037	.052	.065
RATE METH. x 1000 (MOL/gCAT-MIN)	3.286	3.44	2.155	3.03	3.819
RATE SHIFT x 1000 (MOL/gCAT-MIN)	4.691	4.407	3.976	3.346	2.931
FEED PARTIAL PRESSURES (ATM)					
H2	.3	.325	.2	.3	.4
CO	.3	.325	.2	.2	.2
N2	.1	.025	.4	.3	.2
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.3	.325	.2	.2	.2
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.28	.302	.194	.286	.381
CO	.262	.29	.182	.182	.182
N2	.104	.026	.406	.306	.205
CH4	.021	.022	.007	.011	.013
CO2	.029	.028	.014	.012	.01
H2O	.304	.333	.197	.203	.208
CORRECTION FACTOR	.988	.981	1	.995	.989

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	21	22	23	24	25
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	.06	.06	.06	.06	.06
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.113	.083	.08	.082	.097
YIELD OF CH4	.042	.02	.027	.037	.029
RATE METH. x 1000 (MOL/gCAT-MIN)	4.013	.285	.388	.534	.847
RATE SHIFT x 1000 (MOL/gCAT-MIN)	6.708	.92	.784	.657	1.976
FEED PARTIAL PRESSURES (ATM)					
H2	.325	.05	.075	.1	.1
CO	.325	.05	.05	.05	.1
N2	.025	.85	.825	.8	.7
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.325	.05	.05	.05	.1
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.315	.05	.074	.097	.099
CO	.296	.046	.046	.046	.091
N2	.026	.852	.827	.803	.704
CH4	.014	.001	.001	.002	.003
CO2	.024	.003	.003	.002	.007
H2O	.325	.048	.049	.05	.097
CORRECTION FACTOR	.983	.941	.925	.909	.901

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	26	27	28	29	30
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	.06	.06	.06	.06	.06
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.095	.097	.103	.102	.11
YIELD OF CH4	.042	.053	.033	.045	.054
RATE METH. x 1000 (MOL/gCAT-MIN)	1.214	1.553	1.463	1.979	2.347
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.559	1.29	3.044	2.474	2.47
FEED PARTIAL PRESSURES (ATM)					
H2	.15	.2	.15	.225	.3
CO	.1	.1	.15	.15	.15
N2	.65	.6	.55	.475	.4
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.1	.1	.15	.15	.15
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.144	.19	.147	.216	.289
CO	.091	.091	.136	.137	.136
N2	.655	.606	.556	.482	.407
CH4	.004	.005	.005	.007	.008
CO2	.005	.004	.011	.009	.009
H2O	.1	.102	.146	.15	.152
CORRECTION FACTOR	.9	.893	.887	.87	.854

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	31	32	33	34	35
TEMPERATURE (C)	400	400	400	400	500
CATALYST WEIGHT (gr)	.06	.06	.06	.06	.057
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.12	.113	.109	.113	.097
YIELD OF CH4	.064	.052	.038	.04	.016
RATE METH. x 1000 (MOL/gCAT-MIN)	4.311	3.781	2.759	3.495	.978
RATE SHIFT x 1000 (MOL/gCAT-MIN)	3.713	4.489	5.204	6.376	4.974
FEED PARTIAL PRESSURES (ATM)					
H2	.46	.375	.25	.3	.2
CO	.23	.25	.25	.3	.2
N2	.08	.125	.25	.1	.4
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.23	.25	.25	.3	.2
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.441	.361	.244	.293	.208
CO	.209	.228	.227	.273	.182
N2	.082	.128	.255	.102	.403
CH4	.015	.013	.01	.012	.003
CO2	.013	.016	.018	.022	.016
H2O	.239	.254	.246	.297	.188
CORRECTION FACTOR	.842	.837	.831	.827	1

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	36	37	38	39	40
TEMPERATURE (C)	500	500	500	500	500
CATALYST WEIGHT (gr)	.057	.057	.057	.057	.057
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.095	.101	.104	.092	.094
YIELD OF CH4	.027	.04	.024	.012	.023
RATE METH. x 1000 (MOL/gCAT-MIN)	1.66	2.447	2.388	.53	1.051
RATE SHIFT x 1000 (MOL/gCAT-MIN)	4.193	3.769	7.983	3.698	3.292
FEED PARTIAL PRESSURES (ATM)					
H2	.3	.4	.325	.15	.225
CO	.2	.2	.325	.15	.15
N2	.3	.2	.025	.55	.475
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.2	.2	.325	.15	.15
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.301	.395	.333	.157	.227
CO	.183	.183	.296	.137	.137
N2	.303	.203	.025	.552	.478
CH4	.005	.008	.008	.002	.003
CO2	.014	.012	.026	.012	.011
H2O	.194	.199	.312	.14	.144
CORRECTION FACTOR	.985	.971	.958	.992	.985

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	41	42	43	44	45
TEMPERATURE (C)	500	500	500	500	500
CATALYST WEIGHT (gr)	.057	.06	.06	.06	.06
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.1	.126	.121	.117	.12
YIELD OF CH4	.034	.047	.035	.023	.024
RATE METH. x 1000 (MOL/gCAT-MIN)	1.582	3.139	2.489	1.623	2.06
RATE SHIFT x 1000 (MOL/gCAT-MIN)	3.039	5.223	6.211	6.788	8.31
FEED PARTIAL PRESSURES (ATM)					
H2	.3	.46	.375	.25	.3
CO	.15	.23	.25	.25	.3
N2	.4	.08	.125	.25	.1
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.15	.23	.25	.25	.3
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.298	.455	.377	.26	.312
CO	.136	.205	.224	.223	.268
N2	.404	.082	.127	.253	.101
CH4	.005	.011	.009	.006	.007
CO2	.01	.019	.022	.024	.029
H2O	.147	.228	.241	.235	.282
CORRECTION FACTOR	.978	.992	.983	.975	.967

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	46	47	48	49	50
TEMPERATURE (C)	500	500	500	500	500
CATALYST WEIGHT (gr)	.111	.111	.111	.111	.111
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.149	.145	.146	.156	.157
YIELD OF CH4	.012	.021	.039	.019	.032
RATE METH. x 1000 (MOL/gCAT-MIN)	.095	.164	.306	.301	.496
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.072	.974	.839	2.153	1.974
FEED PARTIAL PRESSURES (ATM)					
H2	.05	.075	.1	.1	.15
CO	.05	.05	.05	.1	.1
N2	.85	.825	.8	.7	.65
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.05	.05	.05	.1	.1
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.055	.078	.1	.108	.154
CO	.043	.043	.043	.085	.085
N2	.851	.827	.803	.703	.654
CH4	.001	.001	.002	.002	.003
CO2	.007	.006	.005	.014	.013
H2O	.044	.045	.047	.089	.091
CORRECTION FACTOR	.993	.988	.982	1	1

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	51	52	53	54	55
TEMPERATURE (C)	500	350	350	350	350
CATALYST WEIGHT (gr)	.111	.063	.063	.063	.063
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.154	.094	.101	.103	.108
YIELD OF CH4	.047	.033	.047	.056	.039
RATE METH. x 1000 (MOL/gCAT-MIN)	.737	1.803	2.609	3.094	3.522
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.684	3.386	2.951	2.564	6.139
FEED PARTIAL PRESSURES (ATM)					
H2	.2	.2	.3	.4	.325
CO	.1	.2	.2	.2	.325
N2	.6	.4	.3	.2	.025
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.1	.2	.2	.2	.325
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.198	.195	.288	.384	.317
CO	.085	.184	.183	.184	.298
N2	.606	.405	.306	.205	.026
CH4	.005	.007	.01	.011	.013
CO2	.011	.012	.011	.01	.023
H2O	.095	.197	.203	.207	.324
CORRECTION FACTOR	1	1	1	1	1

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	56	57	58	59	60
TEMPERATURE (C)	350	350	350	350	350
CATALYST WEIGHT (gr)	.063	.063	.063	.063	.063
FEED RATE (SCCM)	390	400	390	390	390
CONVERSION CO	.091	.079	.073	.094	.095
YIELD OF CH4	.025	.03	.037	.032	.043
RATE METH. x 1000 (MOL/gCAT-MIN)	.349	.419	.513	.874	1.183
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.911	.665	.495	1.729	1.426
FEED PARTIAL PRESSURES (ATM)					
H2	.05	.073	.1	.1	.15
CO	.05	.049	.05	.1	.1
N2	.85	.829	.8	.7	.65
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.05	.049	.05	.1	.1
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.05	.071	.097	.097	.144
CO	.046	.045	.047	.091	.091
N2	.852	.832	.803	.704	.656
CH4	.001	.001	.002	.003	.004
CO2	.003	.002	.002	.006	.005
H2O	.048	.048	.05	.098	.1
CORRECTION FACTOR	1	1	1	1	1

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	61	62	63	64	65
TEMPERATURE (C)	350	350	350	350	350
CATALYST WEIGHT (gr)	.063	.065	.065	.065	.065
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.094	.099	.105	.109	.121
YIELD OF CH4	.055	.035	.047	.058	.067
RATE METH. x 1000 (MOL/gCAT-MIN)	1.503	1.385	1.881	2.326	4.106
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.092	2.57	2.326	2.034	3.308
FEED PARTIAL PRESSURES (ATM)					
H2	.2	.15	.225	.3	.46
CO	.1	.15	.15	.15	.23
N2	.6	.55	.475	.4	.08
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.1	.15	.15	.15	.23
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.19	.146	.216	.286	.44
CO	.092	.137	.136	.136	.209
N2	.607	.556	.482	.407	.083
CH4	.006	.005	.007	.009	.016
CO2	.004	.01	.009	.008	.013
H2O	.103	.147	.15	.154	.24
CORRECTION FACTOR	1	1	1	1	1

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	66	67	68	69	70
TEMPERATURE (C)	350	350	350	300	350
CATALYST WEIGHT (gr)	.065	.065	.065	.069	.069
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.124	.114	.12	.086	.125
YIELD OF CH4	.061	.043	.048	.03	.045
RATE METH. x 1000 (MOL/gCAT-MIN)	4.096	2.896	3.819	1.526	2.281
RATE SHIFT x 1000 (MOL/gCAT-MIN)	4.19	4.677	5.764	2.81	4.034
FEED PARTIAL PRESSURES (ATM)					
H2	.375	.25	.3	.2	.2
CO	.25	.25	.3	.2	.2
N2	.125	.25	.1	.4	.4
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.25	.25	.3	.2	.2
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.356	.24	.287	.195	.192
CO	.226	.227	.272	.185	.178
N2	.129	.256	.103	.405	.407
CH4	.016	.011	.015	.006	.009
CO2	.016	.018	.022	.011	.016
H2O	.258	.249	.301	.197	.197
CORRECTION FACTOR	1	1	1	1	1

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	71	72	73	74	75
TEMPERATURE (C)	400	500	300	300	300
CATALYST WEIGHT (gr)	.069	.069	1.234	1.234	1.234
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.125	.105	.62	.62	.636
YIELD OF CH4	.041	.016	.246	.248	.268
RATE METH. x 1000 (MOL/gCAT-MIN)	2.075	.806	.346	.524	.754
RATE SHIFT x 1000 (MOL/gCAT-MIN)	4.235	4.462	.528	.786	1.037
FEED PARTIAL PRESSURES (ATM)					
H2	.2	.2	.1	.15	.2
CO	.2	.2	.1	.15	.2
N2	.4	.4	.7	.55	.4
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.2	.2	.1	.15	.2
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.195	.209	.067	.102	.127
CO	.178	.18	.04	.062	.082
N2	.407	.403	.736	.594	.448
CH4	.008	.003	.026	.04	.06
CO2	.017	.018	.039	.06	.082
H2O	.195	.187	.092	.142	.202
CORRECTION FACTOR	1	1	1	1	1

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	76	77	78	79	80
TEMPERATURE (C)	300	350	350	350	350
CATALYST WEIGHT (gr)	1.234	1.285	1.285	1.285	1.285
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.66	.625	.648	.675	.706
YIELD OF CH4	.28	.225	.24	.256	.285
RATE METH. x 1000 (MOL/gCAT-MIN)	1.185	.305	.487	.692	1.16
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.608	.541	.83	1.135	1.71
FEED PARTIAL PRESSURES (ATM)					
H2	.3	.1	.15	.2	.3
CO	.3	.1	.15	.2	.3
N2	.1	.7	.55	.4	.1
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.3	.1	.15	.2	.3
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.195	.076	.111	.145	.204
CO	.122	.039	.057	.072	.106
N2	.12	.733	.593	.446	.121
CH4	.101	.024	.039	.057	.103
CO2	.137	.042	.066	.093	.152
H2O	.325	.086	.134	.186	.313
CORRECTION FACTOR	1	1	1	1	1

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	81	82	83	84	85
TEMPERATURE (C)	400	400	400	400	500
CATALYST WEIGHT (gr)	.62	.62	.62	.62	.766
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.52	.542	.561	.593	.434
YIELD OF CH4	.17	.192	.205	.226	.078
RATE METH. x 1000 (MOL/gCAT-MIN)	.478	.808	1.149	1.903	.178
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.984	1.475	2.001	3.089	.808
FEED PARTIAL PRESSURES (ATM)					
H2	.1	.15	.2	.3	.1
CO	.1	.15	.2	.3	.1
N2	.7	.55	.4	.1	.7
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.1	.15	.2	.3	.1
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.087	.123	.162	.239	.114
CO	.05	.073	.096	.141	.058
N2	.725	.584	.436	.116	.711
CH4	.018	.031	.045	.078	.008
CO2	.036	.056	.078	.127	.036
H2O	.085	.134	.185	.298	.073
CORRECTION FACTOR	1	1	1	1	1

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	86	87	88	88	88
TEMPERATURE (C)	500	500	500	500	500
CATALYST WEIGHT (gr)	.766	.766	.766	.766	.766
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.474	.501	.541	.541	.541
YIELD OF CH4	.107	.129	.174	.174	.174
RATE METH. x 1000 (MOL/gCAT-MIN)	.366	.587	1.188	1.188	1.188
RATE SHIFT x 1000 (MOL/gCAT-MIN)	1.25	1.69	2.497	2.497	2.497
FEED PARTIAL PRESSURES (ATM)					
H2	.15	.2	.3	.3	.3
CO	.15	.2	.3	.3	.3
N2	.55	.4	.1	.1	.1
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.15	.2	.3	.3	.3
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.162	.208	.283	.283	.283
CO	.082	.105	.154	.154	.154
N2	.568	.422	.112	.112	.112
CH4	.017	.027	.058	.058	.058
CO2	.057	.078	.123	.123	.123
H2O	.115	.16	.271	.271	.271
CORRECTION FACTOR	.986	.973	.96	.96	.96

APPENDIX E

COMPUTER PROGRAMS

APPENDIX E.1

PROCESS CONTROL PROGRAM

```
 10 REM THIS PROGRAM IS DESIGNED TO CONTROL THE SAMPLING OF THE FEED
 20 REM AND PRODUCT STREAMS.  IT ALSO RECORDS THE TEMPERATURES OF THE
 30 REM CATALYST BED AND THE REACTANT GAS IN THE CSTR.
 40 REM
 50 REM
 60 REM
 65 OPENW :7 "$QTO:1"
 66 RESERVE :7
 70 DIM Z1(5), T1(2)
 80 REM POSITION THE SAMPLE VALVE SO THAT THE PROCUCT SAMPLE IS BEING
 90 REM SET-UP
 91 PRINT "ARE SAMPLE VALVES IN 153 POSITION? "
 92 PRINT " (1) YES       (2) NO   "
 93 INPUT P'
 94 IF P'=1 THEN  GOTO 140
100 REM REM
110 DOT(5,8,15)=153
120 WAIT 3
130 DOT(5,8,15)=0
140 REM
142 TASK 1,420
144 TASK 2,590
150 REM
160 REM INPUT THE REACTOR TEMPERATURE SETPOINT
170 PRINT "INPUT THE REACTOR SETPOINT"
180 INPUT T
190 REM
200 FOR I'=1 TO 5
210   READ Z1(I')
220 NEXT I'
230 REM
231 GOTO 330
240 REM CHECK TO SEE IF THE REACTOR IS AT THE SET POINT
250 REM
260 V=AIN(0,6,8)*(1.E06)
270 Q=2.513E-02*V-6.088E-08*V^2+5.536E-13*V^3+9.937E-18*V^4
280 S=5
290 IF ABS(Q-T)<S THEN  GOTO 330
300 PRINT "WAITING 15 MIN. FOR REACTOR TO REACH SET POINT"
310 WAIT 900
320 GOTO 260
330 REM NOW OPEN THE CO,H2,AND THE FEED SAMPLE VALVES
340 REM
350 DOT(5,2,7)=37
360 REM
370 REM
380 PRINT
381 GOTO 590
390 PRINT "THE H2,CO, AND FEED SAMPLE VALVES ARE OPEN"
391 WAIT 600
400 GOTO 590
410 REM
420 REM ************************************************
430 REM                    TASK 1
440 REM ************************************************
450 REM
460 REM DETERMINE IF THE GC IS READY TO SAMPLE.  THIS TASK IS ACTIVATED
470 REM BY TASK 2.
480 REM
490 REM THIS TASK WILL PUT ITS SELF ON HOLD UNTIL THE GC IS READY
500 REM
510 REM
```

```
520 ACTIVATE 1 ON EVENT  (7,2,0)
530 ACTIVATE 2
540 REM
550 REM DISMISS UNTIL ACTIVATED BY TASK 2
560 DISMISS
570 GOTO 520
580 REM
590 REM ********************************************************
600 REM                      TASK 2
610 REM ********************************************************
620 REM
630 REM THIS TASK INJECTS THE FEED AND PRODUCT SAMPLES.
640 REM
650 REM OPEN CHANNEL TO THE PRINTER
670 REM
680 REM CHECK TO SEE IF THE REACTOR IS STILL AT THE SET POINT
690 REM
691 GOTO 880
700 V=AIN(0,6,8)*(1.E06)
800 Q=2.513E-02*V-6.088E-08*V^2+5.536E-13*V^3+9.937E-18*V^4
810 S=5
820 IF ABS(T-Q)<S THEN  GOTO 880
830 PRINT :7
840 PRINT :7 "WAITING 5 MIN. FOR REACTOR TO REACH SET POINT"
850 PRINT :7
860 WAIT 300
870 GOTO 700
880 REM
890 REM RETURN REACTOR TEMPERATURES
900 REM
910 FOR J=1 TO 2
920   V=AIN(0,J*6,8)*(1.E06)
930   T1(J)=2.513E-02*V-6.088E-08*V^2+5.536E-13*V^3+9.937E-18*V^4
940 NEXT J
950 PRINT :7
960 PRINT :7 "TEMPERATURE OF :: BED= ";T1(1);"    GAS= ";T1(2)
970 PRINT :7 "PRODUCT SAMPLE INJECTED AT: ";PTIME :7
971 PRINT :7 "WP"
980 PRINT :7
990 PRINT :7
1000 PRINT :7
1010 REM
1020 REM
1030 DOT(5,8,15)=166
1040 WAIT 3
1050 DOT(5,8,15)=0
1060 REM
1070 REM ACTIVATE TASK 1 AND DISMISS UNTIL
1080 REM THIS TASK IS REACTIVATED BY TASK 1.
1090 REM
1091 GOTO 1120
1100 ACTIVATE 1
1110 DISMISS
1120 REM
1121 PRINT "******************** PRODUCT INJECTED ********************"
1122 WAIT 1800
1123 PRINT
1124 PRINT
1130 REM INJECT FEED SAMPLE
1140 REM
1150 REM CHECK TO SEE THAT THE REACTOR IS AT THE SET POINT
1160 REM
1161 GOTO 1260
1170 V=AIN(0,6,8)*(1.E06)
1180 Q=2.513E-02*V-6.088E-08*V^2+5.536E-13*V^3+9.937E-18*V^4
1190 S=5
```

```
1200 IF ABS(T-Q)<5 THEN  GOTO 1260
1210 PRINT :7
1220 PRINT :7 "WAITING 5 MIN. FOR REACTOR TO REACH SET POINT"
1240 PRINT :7
1250 WAIT 300
1255 GOTO 1170
1260 REM
1270 REM RETURN REACTOR TEMPERATURES
1280 REM
1290 FOR J =1 TO 2
1300   V=AIN(0,J*6,8)*(1.E06)
1310   T1(J)=2.513E-02*V-6.088E-08*V^2+5.536E-13*V^3+9.937E-18*V^4
1320 NEXT J
1330 PRINT :7 "TEMPERATURE OF :: BED= ";T1(1);"      GAS= ";T1(2)
1331 PRINT :7 "FEED SAMPLE INJECTED AT:   ";PTIME :7
1332 PRINT :7 "PF"
1340 PRINT :7
1350 PRINT :7
1360 REM
1370 REM
1380 DOT(5,8,15)=153
1390 WAIT 3
1400 DOT(5,8,15)=0
1410 REM
1420 REM
1430 REM AT THIS POINT THE PROGRAM MAY BE STOPPED.
1440 REM
1450 PRINT :7 "**************************************************"
1460 PRINT :7
1470 REM
1480 REM ACTIVATE TASK 1 AND DISMISS UNTIL THIS TASK IS ACTIVATED
1490 REM AGAIN BY TASK 1.  WHEN ACTIVATED, THE PROGRAM WILL RETURN
1500 REM TO THE TOP OF TASK 2 AND CONTINUE EXECUTION UNTIL STOPPED.
1510 REM
1511 GOTO 1531
1520 ACTIVATE 1
1530 DISMISS
1531 PRINT "********************* FEED INJECTED  *********************"
1532 WAIT 1800
1533 PRINT
1534 PRINT
1540 GOTO 590
1550 END
1560 DATA 0.,2.5132785E-02,-6.0883423E-08,5.5358209E-13
1570 DATA 9.3720918E-18
```

APPENDIX E.2

DATA STORAGE AND ANALYSIS PROGRAM

```
REM THIS PROGRAM CONVERTS THE RAW DATA FROM THE CSTR EXPERIMENTS
REM TO A USEFUL FORM THEN STORES IT IN A RANDOM ACCESS FILE CALLED
REM "REDAT".  ANOTHER PROGRAM CALLED "PRINDAT" WILL ACCESS THIS FILE
REM AND PRINT OUT THE INFORMATION ON A PARTICULAR EXPERIMENTAL RUN.
REM THE DATA IS STORED ACCORDING TO RUN NUMBER (WHICH IS ALSO THE
REM FILE NUMBER).
REM
REM THE DATA IS INPUT THROUTH THE KEY BOARD AND IS STORED ON DISK
REM IN "REDAT"
REM
FILENAMER$="REDAT"
OPEN FILENAMER$ AS #1 LEN=216
NUM=LOF(1)/216
PRINT "THE LAST RUN NUMBER WAS ";NUM
CLOSE #1
REM
REM
10 REM
REM
INPUT "RUN NUMBER=  ";R
INPUT "FLOW H2 (SCCM)=  ";FH
INPUT "FLOW CO (SCCM)=  ";FCO
INPUT "FLOW N2 (SCCM)=  ";F2N
INPUT "FLOW CH4 (SCCM)=  ";FCH4
INPUT "FLOW CO2 (SCCM)=  ";FCO2
INPUT "FLOW FEED SAMPLE (SCCM)=  ";FS
INPUT "FLOW H2O (SCCM)=  ";FW
PRINT ****************************
INPUT "TEMPERATURE OF REACTOR (CELCIUS)=  ";TR
INPUT "CONVERSION OF CO=  ";X
INPUT "YEILD OF CH4=  ";Y
INPUT "WEIGHT OF CATALYST USED (GRAMS)=  ";CATW
INPUT "CONVERSION OF CO and YIELD CH4 AT STANDARD CONDITIONS: START";SC,SD
INPUT "CONVERSION OF CO and YIELD CH4 AT STANDARD CONDITIONS: FINISH";FC,FD
INPUT "TIME OF SET (START, FINISH)";SSET,FSET
INPUT "TIME OF RUN (START, FINISH)";SRUN,FRUN
REM
REM
REM WAT=FW*1239.623
WAT=FW
TFL=WAT+FH+FCO+F2N+FCH4+FCO2
PH2=FH/TFL
PCO=FCO/TFL
PN2=F2N/TFL
PCH4=FCH4/TFL
PCO2=FCO2/TFL
PH2O=WAT/TFL
REM
REM
REM CALCULATE THE OUTLET PARTIAL PRESSURES USING CO AS A BASIS.  TAKE
REM THE FLOW OF CO AS 1.
REM
IH2=FH/FCO
ICH4=FCH4/FCO
ICO2=FCO2/FCO
IN2=F2N/FCO
IH2O=WAT/FCO
SF=FS/FCO
REM
```

```
REM TOTAL PRODUCT FLOW INTO THE REACTOR IS THE SUM OF THE
REM FRACTIONAL FLOWS MINUS TWICE THE YEILD OF CH4
REM
TPF=1+IH2+ICH4+ICO2+IN2+IH2O-2*Y
REM
REM OUTLET PARTIAL PRESSURES
REM
POH2=(IH2-3*Y+(X-Y))/TPF
POCO=(1-X)/TPF
PON2=IN2/TPF
POCH4=(ICH4+Y)/TPF
POCO2=(ICO2+X-Y)/TPF
POH2O=(IH2O+Y-(X-Y))/TPF
REM
REM
REM CALCULATE THE RATE OF METHANATION
REM
FRACT=(1-FS/TFL)
RM=(Y*(FCO*FRACT)/22414)/CATW
REM
REM RATE OF SHIFT
REM
RS=((X-Y)*(FCO*FRACT)/22414)/CATW
CONCO=X
YIELD=Y
TF=TFL*FRACT
TEM=TR
REM
REM THIS PART OF THE PROGRAM INSERTS THE USEFUL DATA INTO THE
REM RANDOM ACCESS FILE "REDAT"
REM
FILETYPE$="DAT"
REM
OPEN FILENAMER$ AS #1 LEN=216
REM
FIELD #1,8 AS H2$,8 AS CO$,8 AS N$,8 AS C4$,8 AS C2$,8 AS HO$,8 AS ZH$,8 AS ZCO$,8 AS ZN$,8
 AS ZC4$,8 AS ZC2$,8 AS ZHO$,8 AS WCO$,8 AS WC4$,8 AS T$,8 AS WCW$,8 AS A$,8 AS B$,8 AS C
$,8 AS D$,8 AS E$,8 AS F$,8 AS G$,8 AS H$,8 AS I$,8 AS J$,8 AS K$
REM
REM
LSET H2$=MKD$(PH2)
LSET CO$=MKD$(PCO)
LSET N$=MKD$(PN2)
LSET C4$=MKD$(PCH4)
LSET C2$=MKD$(PCO2)
LSET HO$=MKD$(PH2O)
LSET ZH$=MKD$(POH2)
LSET ZCO$=MKD$(POCO)
LSET ZN$=MKD$(PON2)
LSET ZC4$=MKD$(POCH4)
LSET ZC2$=MKD$(POCO2)
LSET ZHO$=MKD$(POH2O)
LSET WCO$=MKD$(CONCO)
LSET WC4$=MKD$(YIELD)
LSET T$=MKD$(TEM)
LSET WCW$=MKD$(CATW)
LSET A$=MKD$(RM)
LSET B$=MKD$(RS)
LSET C$=MKD$(TF)
LSET D$=MKD$(SC)
LSET E$=MKD$(FC)
LSET F$=MKD$(SSET)
LSET G$=MKD$(FSET)
LSET H$=MKD$(SRUN)
LSET I$=MKD$(FRUN)
LSET J$=MKD$(SD)
LSET K$=MKD$(FD)
```

```
REM
PUT #1,R
REM
REM
CLOSE #1
REM
REM QUESTION  IS THERE MORE DATA TO BE ENTERED?
REM
PRINT "DO YOU WISH TO ENTER MORE DATA ?  ( YES/NO ) "
INPUT Q$
IF Q$="YES" THEN GOTO 10
999 STOP
END
```

APPENDIX E.3

DATA RETRIEVAL AND PRINTING PROGRAM

```
REM PROGRAM TO PRINT DATA INTO TABLES
REM
DIM A(28,6)
DIM N$(28)
DIM M$(6)
DIM P(6,6)
DIM QP(6,6)
GOTO 200
111 PRINT "ONE RUN NUMBER IS TOO HIGH.  THE LAST RUN WAS ";NUM
PRINT
200 PRINT "WHAT RUN NUMBERS DO YOU WANT DATA FOR? "
PRINT "PUT THE SIX RUN NUMBERS IN THE FORM: A,B,C,D,E,F "
INPUT A(1,1),A(1,2),A(1,3),A(1,4),A(1,5),A(1,6)
REM
FILEMAMER$="REDAT"
OPEN FILEMAMER$ AS #1 LEN=216
NUM=LOF(1)/216
FOR I=1 TO 6
IF NUM< A(1,I) THEN 111
NEXT I
REM
FIELD #1,8 AS H2$,8 AS CO$,8 AS N$,8 AS C4$,8 AS C2$,8 AS HO$,8 AS ZH$,8 AS ZCO$,8 AS ZN$,8
 AS ZC4$,8 AS ZC2$,8 AS ZHO$,8 AS WCO$,8 AS WC4$,8 AS T$,8 AS WCW$,8 AS A$,8 AS B$,8 AS C
$,8 AS D$,8 AS E$,8 AS F$,8 AS G$,8 AS H$,8 AS I$,8 AS J$,8 AS K$
REM
FOR J=1 TO 6
GET #1,A(1,J)
A(2,J)=CVD(T$)
A(3,J)=CVD(WCW$)
A(4,J)=CVD(C$)
A(5,J)=CVD(WCO$)
A(6,J)=CVD(WC4$)
A(7,J)=CVD(A$)
A(8,J)=CVD(B$)
A(9,J)=CVD(H2$)
A(10,J)=CVD(CO$)
A(11 J)=CVD(N$)
A(12,J)=CVD(C4$)
A(13,J)=CVD(C2$)
A(14,J)=CVD(HO$)
A(15,J)=CVD(ZH$)
A(16,J)=CVD(ZCO$)
A(17,J)=CVD(ZN$)
A(18,J)=CVD(ZC4$)
A(19,J)=CVD(ZC2$)
A(20,J)=CVD(ZHO$)
A(21,J)=CVD(D$)
A(22,J)=CVD(J$)
A(23,J)=CVD(E$)
A(24,J)=CVD(K$)
A(25,J)=CVD(F$)
A(26,J)=CVD(G$)
A(27,J)=CVD(H$)
A(28 J)=CVD(I$)
NEXT J
CLOSE #1
```

```
REM
REM ROUND NUMBERS TO 2 DECIMAL PLACES EXCEPT CATALYST WEIGHT
REM CONVERSION, YIELD, AND RATES OF SHIFT AND METHANATION WHICH WILL
REM BE ROUNDED TO 3.
REM
FOR K=1 TO 6
FOR L=3 TO 6
A(L,K)=(INT(10^3*A(L,K)+.5))/10^3
NEXT L
NEXT K
REM
FOR E=1 TO 6
FOR F=7 TO 8
A(F,E)=(INT(10^6*A(F,E)+.5))/10^6
A(F,E)=A(F,E)*1000
NEXT F
NEXT E
REM
FOR F=1 TO 6
FOR G=7 TO 8
A(G,F)=(INT(10^3*A(G,F)+.5))/10^3
NEXT G
NEXT F
FOR W=1 TO 6
A(4,W)=INT(A(4,W)+.5)
NEXT W
REM
FOR M=1 TO 6
FOR N=9 TO 24
A(N,M)=(INT(10^3*A(N,M)+.5))/10^3
NEXT N
NEXT M
REM
FOR P=1 TO 6
FOR Q=25 TO 28
A(Q,P)=INT(A(Q,P))
NEXT Q
NEXT P
REM
REM ASSIGN STRING NAMES TO VARIABLES
REM
N$(1)="RUN NUMBER"
N$(2)="TEMPERATURE (C)"
N$(3)="CATALYST WEIGHT (gr)"
N$(4)="FEED RATE (SCCM)"
N$(5)="CONVERSION CO"
N$(6)="YIELD OF CH4"
N$(7)="RATE METH. x 1000 (MOLE/gCAT-MIN)"
N$(8)="RATE SHIFT x 1000 (MOLE/gCAT-MIN)"
N$(9)="H2"
N$(10)="CO"
N$(11)="N2"
N$(12)="CH4"
N$(13)="CO2"
N$(14)="H2O"
N$(15)="H2"
N$(16)="CO"
N$(17)="N2"
N$(18)="CH4"
N$(19)="CO2"
N$(20)="H2O"
N$(21)="CONVERSION CO START (STD COND.)"
N$(22)="YIELD CH4 START (STD COND.)"
N$(23)="CONVERSION CO FINISH (STD COND.)"
N$(24)="YIELD CH4 FINISH (STD COND.)"
```

```
N$(25)="TIME START SET"
N$(26)="TIME FINISH SET"
N$(27)="TIME START RUN"
N$(28)="TIME FINISH RUN"
REM
REM
REM PRINT DATA INTO TABLE FORM
REM
LPRINT:LPRINT:LPRINT
LPRINT TAB(32);"TABLE OF RESULTS"
LPRINT:LPRINT:LPRINT
LPRINT STRING$(80,"*")
LPRINT "RUN NUMBER";TAB(34); "*";TAB(36); A(1,1);TAB(44); A(1,2);TAB(52); A(1,3);TAB(60);A(1,
4);TAB(68); A(1,5);TAB(76); A(1,6)
LPRINT STRING$(80,"*")
FOR O=2 TO 8
LPRINT N$(O);TAB(34); "*";TAB(36);A(O,1);TAB(44); A(O,2);TAB(52);A(O,3);TAB(60);A(O,4);TAB(6
8); A(O,5);TAB(76); A(O,6)
NEXT O
LPRINT STRING$(80,"*")
LPRINT TAB(26);"FEED PARTIAL PRESSURES (ATM)"
LPRINT STRING$(80,"*")
FOR P=9 TO 14
LPRINT N$(P);TAB(34); "*";TAB(36); A(P,1);TAB(44); A(P,2);TAB(52); A(P,3);TAB(60); A(P,4);TAB(
68); A(P,5);TAB(76); A(P,6)
NEXT P
LPRINT STRING$(80,"*")
LPRINT TAB(25);"PRODUCT PARTIAL PRESSURES (ATM)"
LPRINT STRING$(80,"*")
FOR V=15 TO 20
LPRINT N$(V);TAB(34); "*";TAB(36); A(V,1);TAB(44); A(V,2);TAB(52); A(V,3);TAB(60); A(V,4);TAB
(68); A(V,5);TAB(76); A(V,6)
NEXT V
LPRINT STRING$(80,"*")
LPRINT TAB(33);"ACTIVITY DATA"
LPRINT STRING$(80,"*")
FOR W=21 TO 28
LPRINT N$(W);TAB(34);"*";TAB(36);A(W,1);TAB(44);A(W,2);TAB(52);A(W,3);TAB(60);A(W,4);TAB(6
8);A(W,5);TAB(76);A(W,6)
NEXT W
FOR WER=1 TO 20
LPRINT
NEXT WER
STOP
END
```

APPENDIX F

LIFETIME STUDY DATA

APPENDIX F.1

0.5% Rh 400°C

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	168	169	170	171	172
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	1.524	1.524	1.524	1.524	1.524
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.318	.307	.298	.289	.287
YIELD OF CH4	.185	.189	.179	.179	.177
RATE METH. x 1000 (MOL/gCAT-MIN)	.634	.647	.613	.614	.607
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.455	.404	.406	.377	.377
FEED PARTIAL PRESSURES (ATM)					
H2	.3	.3	.3	.3	.3
CO	.3	.3	.3	.3	.3
N2	.1	.1	.1	.1	.1
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.3	.3	.3	.3	.3
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.195	.187	.196	.192	.194
CO	.23	.235	.236	.239	.239
N2	.113	.113	.112	.112	.112
CH4	.063	.064	.06	.06	.06
CO2	.045	.04	.04	.037	.037
H2O	.355	.362	.356	.359	.358
TIME OF SAMPLE (hr)	1	11	23	34	46

TABLE OF EXPERIMENTAL RESULTS
0.5% RHODIUM CATALYST

RUN NUMBER	173	174	175	176	177
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	1.524	1.524	1.524	1.524	1.524
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.277	.275	.278	.274	.272
YIELD OF CH4	.173	.172	.178	.173	.173
RATE METH. x 1000 (MOL/gCAT-MIN)	.592	.59	.609	.591	.594
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.356	.351	.344	.348	.338
FEED PARTIAL PRESSURES (ATM)					
H2	.3	.3	.3	.3	.3
CO	.3	.3	.3	.3	.3
N2	.1	.1	.1	.1	.1
CH4	0	0	0	0	0
CO2	0	0	0	0	0
H2O	.3	.3	.3	.3	.3
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.196	.196	.191	.195	.194
CO	.242	.243	.242	.243	.244
N2	.112	.112	.112	.112	.112
CH4	.058	.058	.06	.058	.058
CO2	.035	.034	.034	.034	.033
H2O	.358	.358	.362	.358	.36
TIME OF SAMPLE (hr)	57	67	80	90	97

APPENDIX F.2

70% Ni 300°C

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	89	90	91	92	93
TEMPERATURE (C)	300	300	300	300	300
CATALYST WEIGHT (gr)	6.043	6.043	6.043	6.043	6.043
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.888	.88	.89	.881	.877
YIELD OF CH4	.47	.465	.475	.465	.468
RATE METH. x 1000 (MOL/gCAT-MIN)	.257	.255	.26	.254	.256
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.229	.227	.227	.228	.224
FEED PARTIAL PRESSURES (ATM)					
H2	.285	.285	.285	.285	.285
CO	.19	.19	.19	.19	.19
N2	.05	.05	.05	.05	.05
CH4	.095	.095	.095	.095	.095
CO2	.19	.19	.19	.19	.19
H2O	.19	.19	.19	.19	.19
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.117	.12	.114	.121	.117
CO	.026	.028	.026	.028	.028
N2	.061	.061	.061	.061	.061
CH4	.224	.223	.226	.223	.224
CO2	.328	.326	.328	.327	.326
H2O	.243	.243	.246	.242	.245
TIME OF SAMPLE (hr)	2	14	20	40	56

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	94	95	96	97	98
TEMPERATURE (C)	300	300	300	300	300
CATALYST WEIGHT (gr)	6.043	6.043	6.043	6.043	6.043
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.874	.851	.872	.868	.872
YIELD OF CH4	.485	.474	.479	.498	.51
RATE METH. x 1000 (MOL/gCAT-MIN)	.265	.259	.262	.273	.279
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.213	.206	.215	.202	.198
FEED PARTIAL PRESSURES (ATM)					
H2	.285	.285	.285	.285	.285
CO	.19	.19	.19	.19	.19
N2	.05	.05	.05	.05	.05
CH4	.095	.095	.095	.095	.095
CO2	.19	.19	.19	.19	.19
H2O	.19	.19	.19	.19	.19
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.101	.105	.106	.088	.078
CO	.029	.035	.03	.031	.03
N2	.061	.061	.061	.062	.062
CH4	.229	.226	.227	.234	.238
CO2	.324	.319	.324	.321	.321
H2O	.255	.254	.252	.265	.27
TIME OF SAMPLE (hr)	76	96	118	136	156

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	*	99	100	101	102	103
TEMPERATURE (C)	*	300	300	300	300	300
CATALYST WEIGHT (gr)	*	6.043	6.043	6.043	6.043	6.043
FEED RATE (SCCM)	*	390	390	390	390	390
CONVERSION CO	*	.859	.861	.862	.852	.863
YIELD OF CH4	*	.506	.506	.51	.504	.52
RATE METH. x 1000 (MOL/gCAT-MIN)	*	.277	.277	.279	.276	.284
RATE SHIFT x 1000 (MOL/gCAT-MIN)	*	.193	.195	.192	.191	.188
FEED PARTIAL PRESSURES (ATM)						
H2	*	.285	.285	.285	.285	.285
CO	*	.19	.19	.19	.19	.19
N2	*	.05	.05	.05	.05	.05
CH4	*	.095	.095	.095	.095	.095
CO2	*	.19	.19	.19	.19	.19
H2O	*	.19	.19	.19	.19	.19
PRODUCT PARTIAL PRESSURES (ATM)						
H2	*	.078	.08	.076	.079	.067
CO	*	.033	.033	.033	.035	.032
N2	*	.062	.062	.062	.062	.062
CH4	*	.237	.236	.238	.236	.241
CO2	*	.318	.319	.319	.317	.318
H2O	*	.271	.27	.273	.271	.279
TIME OF SAMPLE (hr)	*	176	196	216	250	263

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	104	105	106	119	120
TEMPERATURE (C)	300	300	300	300	300
CATALYST WEIGHT (gr)	6.043	6.043	6.043	6.043	6.043
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.856	.867	.868	.867	.869
YIELD OF CH4	.509	.503	.502	.462	.503
RATE METH. x 1000 (MOL/gCAT-MIN)	.278	.275	.275	.253	.275
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.19	.199	.2	.222	.2
FEED PARTIAL PRESSURES (ATM)					
H2	.285	.285	.285	.285	.285
CO	.19	.19	.19	.19	.19
N2	.05	.05	.05	.05	.05
CH4	.095	.095	.095	.095	.095
CO2	.19	.19	.19	.19	.19
H2O	.19	.19	.19	.19	.19
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.076	.083	.085	.12	.084
CO	.034	.031	.031	.031	.031
N2	.062	.062	.062	.061	.062
CH4	.238	.236	.235	.222	.236
CO2	.317	.32	.321	.324	.321
H2O	.274	.268	.267	.244	.267
TIME OF SAMPLE (hr)	271	307	318	30	300

APPENDIX F.3

70% Ni 350°C

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	118	135	136	137	138
TEMPERATURE (C)	350	350	350	350	350
CATALYST WEIGHT (gr)	4.461	4.461	4.461	4.461	4.461
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.858	.859	.857	.849	.859
YIELD OF CH4	.459	.469	.455	.443	.46
RATE METH. x 1000 (MOL/gCAT-MIN)	.34	.347	.337	.329	.341
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.295	.289	.298	.3	.295
FEED PARTIAL PRESSURES (ATM)					
H2	.285	.285	.285	.285	.285
CO	.19	.19	.19	.19	.19
N2	.05	.05	.05	.05	.05
CH4	.095	.095	.095	.095	.095
CO2	.19	.19	.19	.19	.19
H2O	.19	.19	.19	.19	.19
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.12	.112	.123	.131	.119
CO	.033	.033	.033	.035	.033
N2	.061	.061	.06	.06	.061
CH4	.221	.224	.219	.216	.221
CO2	.322	.321	.322	.321	.322
H2O	.244	.249	.242	.237	.244
TIME OF SAMPLE (hr)	234	4	50	60	80

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	113	114	115	116	117
TEMPERATURE (C)	350	350	350	350	350
CATALYST WEIGHT (gr)	4.461	4.461	4.461	4.461	4.461
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.86	.858	.86	.858	.855
YIELD OF CH4	.457	.466	.456	.451	.451
RATE METH. x 1000 (MOL/gCAT-MIN)	.339	.345	.338	.334	.334
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.299	.291	.3	.301	.299
FEED PARTIAL PRESSURES (ATM)					
H2	.285	.285	.285	.285	.285
CO	.19	.19	.19	.19	.19
N2	.05	.05	.05	.05	.05
CH4	.095	.095	.095	.095	.095
CO2	.19	.19	.19	.19	.19
H2O	.19	.19	.19	.19	.19
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.122	.114	.123	.127	.126
CO	.032	.033	.032	.033	.033
N2	.061	.061	.06	.06	.06
CH4	.22	.223	.22	.218	.218
CO2	.323	.321	.323	.323	.322
H2O	.242	.248	.242	.24	.24
TIME OF SAMPLE (hr)	16	20	35	73	102

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	139	140	141	142	143
TEMPERATURE (C)	350	350	350	350	350
CATALYST WEIGHT (gr)	4.461	4.461	4.461	4.461	4.461
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.858	.855	.858	.85	.857
YIELD OF CH4	.453	.467	.45	.459	.458
RATE METH. x 1000 (MOL/gCAT-MIN)	.336	.346	.333	.34	.339
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.3	.288	.302	.29	.296
FEED PARTIAL PRESSURES (ATM)					
H2	.285	.285	.285	.285	.285
CO	.19	.19	.19	.19	.19
N2	.05	.05	.05	.05	.05
CH4	.095	.095	.095	.095	.095
CO2	.19	.19	.19	.19	.19
H2O	.19	.19	.19	.19	.19
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.125	.113	.128	.118	.121
CO	.033	.033	.033	.034	.033
N2	.06	.061	.06	.061	.061
CH4	.219	.223	.218	.221	.22
CO2	.322	.321	.323	.32	.322
H2O	.241	.249	.239	.246	.244
TIME OF SAMPLE (hr)	120	140	160	180	200

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	144	145	146	147	148
TEMPERATURE (C)	350	350	350	350	350
CATALYST WEIGHT (gr)	4.461	4.461	4.461	4.461	4.461
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.857	.858	.858	.853	.852
YIELD OF CH4	.452	.457	.45	.457	.466
RATE METH. x 1000 (MOL/gCAT-MIN)	.335	.339	.334	.338	.346
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.3	.297	.302	.294	.286
FEED PARTIAL PRESSURES (ATM)					
H2	.285	.285	.285	.285	.285
CO	.19	.19	.19	.19	.19
N2	.05	.05	.05	.05	.05
CH4	.095	.095	.095	.095	.095
CO2	.19	.19	.19	.19	.19
H2O	.19	.19	.19	.19	.19
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.126	.122	.128	.121	.112
CO	.033	.033	.033	.034	.034
N2	.06	.061	.06	.06	.061
CH4	.218	.22	.218	.22	.223
CO2	.322	.322	.323	.321	.32
H2O	.24	.243	.239	.244	.25
TIME OF SAMPLE (hr)	220	244	266	280	300

APPENDIX F.4

70% Ni 400°C

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	107	108	109	110	111
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	5.302	5.302	5.302	5.302	5.302
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.817	.813	.81	.792	.81
YIELD OF CH4	.407	.409	.415	.404	.411
RATE METH. x 1000 (MOL/gCAT-MIN)	.254	.255	.259	.252	.256
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.255	.252	.246	.242	.249
FEED PARTIAL PRESSURES (ATM)					
H2	.285	.285	.285	.285	.285
CO	.19	.19	.19	.19	.19
N2	.05	.05	.05	.05	.05
CH4	.095	.095	.095	.095	.095
CO2	.19	.19	.19	.19	.19
H2O	.19	.19	.19	.19	.19
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.155	.152	.147	.152	.15
CO	.041	.042	.043	.047	.043
N2	.059	.059	.059	.059	.059
CH4	.204	.204	.206	.203	.205
CO2	.317	.316	.315	.312	.315
H2O	.224	.226	.23	.228	.228
TIME OF SAMPLE (hr)	12	74	150	200	250

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	112	121	122	123	124
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	5.302	5.302	5.302	5.302	5.302
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.809	.815	.816	.821	.81
YIELD OF CH4	.411	.413	.409	.394	.411
RATE METH. x 1000 (MOL/gCAT-MIN)	.256	.257	.255	.246	.256
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.248	.251	.254	.266	.249
FEED PARTIAL PRESSURES (ATM)					
H2	.285	.285	.285	.285	.285
CO	.19	.19	.19	.19	.19
N2	.05	.05	.05	.05	.05
CH4	.095	.095	.095	.095	.095
CO2	.19	.19	.19	.19	.19
H2O	.19	.19	.19	.19	.19
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.15	.15	.153	.166	.15
CO	.043	.042	.041	.04	.043
N2	.059	.059	.059	.059	.059
CH4	.205	.206	.204	.2	.205
CO2	.315	.316	.317	.319	.315
H2O	.228	.228	.225	.216	.228
TIME OF SAMPLE (hr)	294	20	30	50	80

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	125	126	127	128	129
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	5.302	5.302	5.302	5.302	5.302
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.816	.815	.81	.797	.812
YIELD OF CH4	.409	.408	.414	.403	.415
RATE METH. x 1000 (MOL/gCAT-MIN)	.255	.254	.258	.251	.259
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.254	.254	.247	.246	.248
FEED PARTIAL PRESSURES (ATM)					
H2	.285	.285	.285	.285	.285
CO	.19	.19	.19	.19	.19
N2	.05	.05	.05	.05	.05
CH4	.095	.095	.095	.095	.095
CO2	.19	.19	.19	.19	.19
H2O	.19	.19	.19	.19	.19
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.153	.154	.147	.154	.147
CO	.041	.042	.043	.046	.042
N2	.059	.059	.059	.059	.059
CH4	.205	.204	.206	.203	.206
CO2	.317	.316	.315	.313	.315
H2O	.226	.225	.23	.226	.23
TIME OF SAMPLE (hr)	101	120	135	160	180

TABLE OF EXPERIMENTAL RESULTS
70% NICKEL CATALYST

RUN NUMBER	130	131	132	133	134
TEMPERATURE (C)	400	400	400	400	400
CATALYST WEIGHT (gr)	5.302	5.302	5.302	5.302	5.302
FEED RATE (SCCM)	390	390	390	390	390
CONVERSION CO	.8	.808	.805	.793	.809
YIELD OF CH4	.402	.411	.418	.412	.408
RATE METH. x 1000 (MOL/gCAT-MIN)	.25	.256	.26	.257	.254
RATE SHIFT x 1000 (MOL/gCAT-MIN)	.248	.248	.242	.238	.25
FEED PARTIAL PRESSURES (ATM)					
H2	.285	.285	.285	.285	.285
CO	.19	.19	.19	.19	.19
N2	.05	.05	.05	.05	.05
CH4	.095	.095	.095	.095	.095
CO2	.19	.19	.19	.19	.19
H2O	.19	.19	.19	.19	.19
PRODUCT PARTIAL PRESSURES (ATM)					
H2	.156	.15	.143	.146	.152
CO	.045	.043	.044	.047	.043
N2	.059	.059	.059	.059	.059
CH4	.202	.205	.207	.205	.204
CO2	.314	.315	.313	.311	.315
H2O	.225	.228	.233	.232	.226
TIME OF SAMPLE (hr)	220	235	260	270	280

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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The utilization of carbon dioxide reforming of methane in a solar based Chemical Energy Transmission System (CETS) relies greatly upon the development of suitable catalysts for both the endothermic and exothermic reactions. Carbon dioxide reforming of methane produces hydrogen and carbon monoxide at a ratio of about one, thus requiring the methanation reaction on the other sice of the closed loop CETS to utilixe this feed. H_2/CO ratios lower than three favor the formation of carbon with industrial methanation catalysts. Preliminary tests performed on methanation with rhodium and nickel catalysts produced two, 0.5% Rh/Al_2O_3 and Ni/Al_2O_3, for further study.

Kinetic experiments were conducted in an isothermal continuous stirred tank reactor constructed of a copper alloy which prevented carbon formation on reactor parts. These experiments were performed on pelleted 0.5% Rh/Al_2O_3 in the 400 to 500°C range and pelleted 70% Ni/Al_2O_3 in the 300 to 500°C temperature range. In most experiments steam was added to the reactor feed to inhibit carbon formation. Langmuir-Hinshelwood expressions were fitted

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